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# NATO ADVANCED RESEARCH WORKSHOP

## *ORGANIC NANOPHOTONICS*



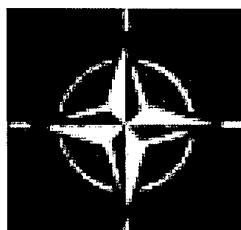
*Aix-en-Provence (France), August 25-29, 2002*

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## We wish to thank the following for their contribution to the success of this workshop

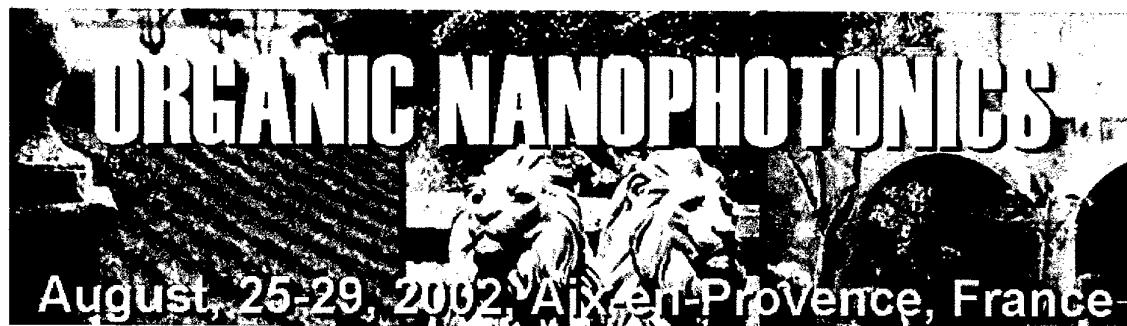
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## NATO ADVANCED RESEARCH WORKSHOP PROGRAM

### **Sunday 25<sup>th</sup>**

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16:30-17:00 *Welcome coffee*

17:00-17:20 *Welcome address*

Vladimir M AGRANOVICH  
Fabrice CHARRA  
François KAJZAR

#### *Introductory session* *chair: Vladimir. AGRANOVICH*

17:20-18:00 Nanophotonics: A new frontier

Paras N. PRASAD

Plenary talk

18:00-18:30 AFOSR Interests in Organic Nanophotonics

Charles W. LEE

18:30-19:00 Organic Spintronics: a new perspective for organic semiconductors

Carlo TALIANI

19:00-19:30 Optical properties and energy transport in dendrimers

Peter REINEKER

20:00 *Dinner*

## **Monday 26<sup>th</sup> morning**

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### *Single molecule devices* chair: *François KAJZAR*

8:00-8:40	Photoswitchable molecular and supra-molecular receptors	Michael V ALFIMOV
Plenary talk		
8:40-9:10	Molecules with moving parts: hydrogen bond-assembled molecular machinery	David A. LEIGH
9:10-9:40	Polymeric $\beta$ -dicarbonyl compounds as structural basis for intelligent systems with multifunctional nature	Ivan PETKOV
9:40-10:00	Quantum chemical first-principle design of single supermolecule Photoactive Machines and Molecular classical and quantum logic devices	Arvydas TAMULIS
10:00-10:30	<i>Coffee break</i>	

### *Photonics at surfaces* chair: *Paras N. PRASAD*

10:30-11:00	STM-induced photon emission	Richard BERNDT
11:00-11:30	STM-induced light emission from single-nanoparticles and molecules	Fabrice CHARRA
11:30-12:00	Optical properties of ultrathin epitaxial films of PTCDA on Au(111)	Torsten FRITZ
12:00-12:20	Scanning tunneling microscopy of long-chain organic molecules at the liquid/solid interface	Oleksander MARCHENKO

## **Monday 26<sup>th</sup> afternoon**

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16:30-17:00 *Coffee break*

### *Macromolecules I* chair: *Toshikuni KAINO*

17:00-17:40	Electronics, fluidics, and biology : new horizons Plenary talk and opportunities for Nanoscale optics	James T. YARDLEY
17:40-18:10	Highly efficient two-photon absorbing dendritic molecules	Kwang-Sup LEE
18:10-18:30	Investigation of optical excitations in novel dendrimers using ultra fast anisotropy measurements	Mahinda I. RANASINGHE
18:30-18:50	New organic dendrimers with greatly enhanced multi-photon absorption for photonics applications	Charles W. SPANGLER
18:50-19:10	Dendritic polymers for optical applications	Anders HULT
19:10-19:30	Optical excitations in novel dendritic architectures	Oleg P. VARNAVSKI

20:00 *Dinner*

## **Monday 26<sup>th</sup> evening**

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### *Poster session I*

21:00-21:30	Introduction of posters by their authors (see poster list at the end of program)
21:30-23:30	Poster session

## **Tuesday 27<sup>th</sup> morning**

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### *Nanostructured photonic devices* *chair: Fabrice CHARRA*

8:00-8:40	Challenges in nanostructured organic electronic devices	Stephen R. FORREST
Plenary talk		
8:40-9:10	Laser-assisted scanning tunneling spectroscopy: a new tool to probe local photocarriers in organic photoconductors	Denis FICHOU
9:10-9:30	Organic-inorganic nanocomposites for solar cell devices	Claire PITOIS
9:30-9:50	Electronic properties and the magnetic behaviour of hybride organic-inorganic advanced materials	Ana EMANDI
9:50-10:05	<i>Coffee break</i>	

### *Self-assembly* *chair: Natalie KAMANINA*

10:05-10:35	Nanoprecise self-assembly of electro-optic and electroluminescent molecular arrays	Tobin J. MARKS
10:35-11:05	Aggregation control of fluorescent dyes in mesoscopic dome structures	Olaf KARTHAUS
11:05-11:25	Intercalation of Rhodamine B in Molybdenum Disulfide	Guillermo GONZALEZ
11:25-11:45	Nonlinear optical properties of self-assembled molecular J-aggregates of pseudoisocyanine in nanometer films	Alexander I PLEKHANOV
11:45-12:05	Opto-electronic properties of discotic materials	Jacek ULANSKI

## **Tuesday 27<sup>th</sup> afternoon**

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13:30	<i>Departure for afternoon excursion</i>
20:00	<i>Dinner</i>

## **Wednesday 28<sup>th</sup> morning**

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### *Confined photons and excitons* chair: *Carlo TALIANI*

8:00-8:40	Microcavity polaritons in disordered organics	Vladimir M. AGRANOVICH
Plenary talk		
8:40-9:10	Organic and metallic photonic crystal nanostructures for tunable photonic devices	Anvar ZAKHIDOV
9:10-9:40	Hyperpolar multichromophoric nanoassembly for molecular nonlinear optics	Mireille BLANCHARD-DESCE
9:40-10:00	Photoinduced spontaneous patterning of azopolymer films: towards a new process for nanostructuration	Christophe HUBERT

10:00-10:30 *Coffee break*

### *Subwavelength photonics* chair: *Pierre-Alain CHOLLET*

10:30-11:00	Sub-microscopic nonlinear optical probing of organized molecular assemblies	Sophie BRASSELET
11:00-11:30	Investigation of anomalous light propagation in discrete optical media	Andreas BRAÜER
11:30-11:50	All optically induced frequency doubling process with periodic modulation of the nonlinear susceptibilities	Aleksandra APOSTOLUK
11:50-12:10	Characterization of nonlinear optical parameters of metal-doped polyvinylpyrrolidone nanostructures and organic dye molecules	Rashid A GANEEV
12:10-12:30	Novel heterocycle-based two-photon absorbing dyes	Alessandro ABBOTTO

## **Wednesday 28<sup>th</sup> afternoon**

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16:30-17:00 *Coffee break*

### *Macromolecules II* *chair: Juliusz SWORAKOWSKI*

17:00-17:40	Related Photo, Thermal, and Charge Injection	Ray H. BAUGHMAN
Plenary talk	Driven Processes and Devices Based on Single Walled Carbon Nanotubes	
17:40-18:10	Nonlinear optical study of fullerene-doped conjugated systems: a new material for nanophotonics applications	Natalie V. KAMANINA
18:10-18:40	Conduction and optical properties of DNA	Esther M. CONWELL
18:40-19:10	Dynamics of Eosin Y encapsulated in a fourth generation functionalised POPAM dendrimer	Francesco ZERBETTO
19:10-19:30	Protein nanostructures light control for data storage	Patrick MEYRUEIS

20:00 *Dinner*

## **Wednesday 28<sup>th</sup> evening**

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### *Poster session II*

21:00-23:30 *Poster session (see poster list at the end of the program)*

## Thursday 29<sup>th</sup>

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### *Single-molecule photophysics* chair: Ray BAUGHMAN

8:00-8:30	Localizing single molecules and watching them interact	Vahid SANDOGHDAR
8:30-8:50	Photon statistics of a triggered single photon source	François TREUSSART
8:50-9:10	Single molecule current switch – state of art	Stanislav NEŠPUREK
9:10-9:30	Electroactive molecular devices with carrier mobilities modulated by light – an electrostatic approach	Juliusz SWORAKOWSKI
9:30-9:50	Fluorescent photochromic diarylethene oligomers	Eunkyoung KIM
9:50-10:20	<i>Coffee break</i>	

### *Photochromism and photoreactive molecules* chair: James YARDLEY

10:20-10:50	Photoreactive calixarene polymers for photonics applications	Toshikuni KAINO
10:50-11:20	The search for highly polar betainic type molecules for electro-optical applications	Ojars NEILANDS
11:20-11:50	Intermolecular charge transfer multilayers for NLO applications	François KAJZAR
11:50-12:10	Two-photon isomerization of diaryethenes in films of poly-methyl-methacrylate	Zouheir SEKKAT
12:10-12:30	Photosensitivity of some pentazadiene-1,4	Olena O. NOVIKOVA

### *Conclusion and perspectives*

12:30	Concluding remarks	Vladimir M AGRANOVICH Fabrice CHARRA François KAJZAR
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## POSTERS

Poster 1	Real-time control of the all-optical poling process in polymer thin films	Aleksandra APOSTOLUK
Poster 2	Molecular probes for nonlinear optical imaging of biological membranes	Mireille BLANCHARD-DESCE
Poster 3	Mapping the dipolar radiation of copper nanoparticles using a photosensitive film	Pierre-Alain CHOLLET
Poster 4	Magnetic and morphologic characterization of some substituted ferrites synthesized by a non-conventional method	Elena CRISTUREAN
Poster 5	The investigation of the surface potential of betaine-type dipolar doped polymeric films	Rorijs DOBULANS
Poster 6	3D Characterization of Molecular Photo-Orientation: Application to All-Optical Poling and Liquid Crystal Polymers	Michel DUMONT
Poster 7	Collision induced light scattering of SF6 - isotropic and anisotropic spectra	K NOWICKA
Poster 8	Secure Holographic System with Polarization Encryption using Bacteriorhodopsin	Yoshiko OKADA-SHUDO
Poster 9	STM-induced photon emission at liquid-solid interface	Karen PERRONET
Poster 10	Control of light emission properties of diodes by surface patterning	Licinio ROCHA
Poster 11	Donor-acceptor dyes for advanced photonic applications	Raffaella SIGNORINI
Poster 12	Charge transfer in molecular logic devices possessing different molecular bridges	Jelena TAMULIENE
Poster 13	Dendritic polyesters for optical limiting applications	Robert VESTBERG
Poster 14	Low-molecular-weight organic glass exhibiting photochromism and second-order nonlinear optical activity	Elena ISHOW

# ORAL PRESENTATIONS



# Nanophotonics: A New Frontier

Paras N. Prasad

*Institute for Lasers, Photonics and Biophotonics*

*Departments of Chemistry, Physics, Electrical Engineering and Medicine*

*State University of New York at Buffalo, Buffalo New York 14260*

Today, major scientific breakthrough frequently occurs at the interface between various disciplines. Nanophotonics defined as nanoscale optical science and technology is the interface between Photonics and NanoScience and Technology. It is a new frontier offering challenging opportunities for studying fundamental processes of interaction between the radiation field and matter on a scale much smaller than the wavelength of radiation as well as for design of novel nanostructured optical materials, synthesis and processing.

Furthermore, the use of such confined interactions to spatially localized photochemical processes also offers exciting technological opportunities for nanofabrication. Selected examples of our studies in each of these areas will be presented:

i) nonlinear optical interactions involving nanoscale confinement of radiation are theoretically analyzed and experimentally probed using a near-field geometry,

ii) nanoscale confined optical domains to control excitation dynamics and energy transfer and to produce photon localization are illustrated by examples of new nanostructured materials such as rare-earth doped glasses,

iii) multiphasic inorganic: organic hybrid nano-composites, and photonic crystals.

One application of nanophotonics utilizes spatially localized photochemistry using near-field excitation for nanofabrication and nanoscale memory.

A new concept involving both photonics and nanotechnology for biophotonics is that of a nanoclinic for optical diagnostic and targeted therapy. A chemical approach is used to create this nanoclinic which consists of a 10-40 nm silica bubble containing optical diagnostic tools and drug delivery systems and functionalized on its surface with targeting groups to carry it selectively to a diseased cell.

The talk will conclude with a discussion of future outlooks for Nanophotonics.

## AFOSR Interests in Organic Nanophotonics

Charles Lee

*AFOSR/NL  
Arlington, VA  
USA*

The Polymer Chemistry Program at AFOSR has supported research relating to Nanotechnology in Organics and Polymers in the last decade. The supported research included block copolymers and polymer blends with nanoscale phase separation. Properties of interests include mechanical properties, photonics and electronic properties. This area of interest is further supported since 1966 under a Multidisciplinary University Research Initiative (MURI) on Polymeric Nanostructures. This effort ended in 2001.

Under the Defense University Research Initiative on NanoTechnology (DURINT), a new effort on Organic Nanophotonics and Nanoelectronics was started in 2001. This effort is headed by Buffalo University, teaming with University of Washington, University of California, Berkeley, Yale University and Massachusetts Institute of Technology.

The objective of this effort is to develop device-design methodologies at the molecular and nanoscopic levels for producing new materials/structures to yield future generation information technology.

The research approaches include gaining a fundamental understanding of the chemistry and physics of organic-based nanostructures, developing new classes of materials and structures for molecular electronics, nanoelectronics, nanophotonics and nano-optoelectronics, utilizing theoretical guidance and synthetic strategies for new molecular design, and creating periodic or aperiodic nanostructures by a number of approaches.

# Organic Spintronics: a new perspective for organic semiconductors

I Bergenti, V. Dedi, P. Nozar, G. Ruani, M. Murgia and C. Taliani

*ISMN-Bo, CNR, Via P. Gobetti, 101, 40129, Bologna, Italy*

In Spintronics the electronic information is stored, transmitted and read via electrical carrier spin polarisation (SP). Spintronics devices are based on the generation of charge carrier SP in an active medium and in the spin-polarisation detection at the output. We explore a new approach to Spintronics by using organic semiconductors as active transport materials in combination with novel Colossal Magnetoresistance (CMR) metal electrodes. SP injector and spin analyser are made by a  $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$  (LSMO) thin film which is ferromagnetic with 100% SP at room temperature. LSMO is a poor metal characterised by a narrow band ( $<1$  eV) and a small number of carriers (approx.  $10^{21}\text{cm}^{-3}$ ) like in high temperature cuprate superconductors and organic metals.

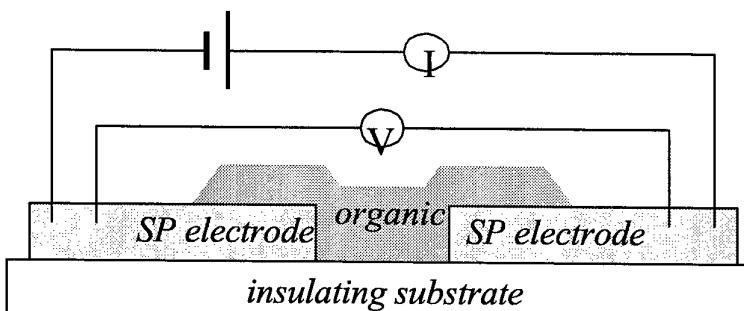


Fig.1 Planar device structures with two CMR SP electrodes separated by 70-500 nm are fabricated by electron-beam lithography and the organic semiconductor (sexithienyl ( $T_6$ )) is deposited by vacuum evaporation in UHV.

At zero magnetic field the electrodes SP are randomly oriented while in the magnetic field they orient in parallel. By inserting a 3.4 kOe magnetic field we observe a strong decrease of the resistance. The negative magnetoresistance (MR) signal is nearly 30% for a gap of 140 nm. By increasing the gap the MR decreases to 7-10% at 200-nm and eventually vanishes at 300 nm. The room temperature spin transfer coherence length is estimated to be about 200-300 nm in  $T_6$ . Electrical resistivity of  $10^6$  Ohm cm indicates that the films are indeed doped by ambient oxygen atmosphere. To the best of our knowledge this is the first evidence of spin coherent injection and transfer in organic semiconductors (1). The ambient condition operation of this process opens the possibility of practical applications as for instance in low power spin-valve memory devices. The benefit of SP injection may also be applied in organic optoelectronics, as in OLED, since the spin statistics of radiative carrier recombination may be altered by inducing the preferential formation of allowed singlet excitons. Preliminary results in OLED configuration indeed show efficient charge injection and electroluminescence.

1- V. Dedi et. al., Sol. St. Commun., **122**, (2002), 181; USA patent n°: 6.325.914.

# Optical Properties and Energy Transport in Dendrimers

Peter Reineker<sup>1</sup>, A. Engelmann<sup>1</sup>, V. I. Yudson<sup>2,3</sup>

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<sup>3</sup>*Center for Frontier Science, Chiba University, Chiba 263-8522, Japan*

Dendrimers are tree-like branched molecules with a diameter on the nano-scale. In recent years these molecules have been the subject of increasing experimental and theoretical interest. For these nano-structures a broad range of applications in biology, chemistry, and physics seems to appear. From a theoretical point of view many questions are open: To which extent is the idealized tree-like structure realized in nature, to which extent are the molecules coiled up or otherwise disturbed? Are the electronic excitations coherent or incoherent? Which part of the molecules is excited after irradiating with light?

As starting point to answer these questions we model the hyperbranched molecule by an ensemble of two-level systems with different excitation energies in each generation of the dendrimer. The molecules are interacting with each other via transfer integrals modeling the specific spatial structure of the dendrimers. The influence of the phonons is taken into account in a stochastic manner by allowing for fluctuations of the local excitation energies and of the transfer matrix elements. We calculate the optical absorption line shape for dendrimers of various sizes and discuss the spatial distribution of the excitation energy as a function of the dendrimer size. Furthermore, the time dependence of the coupled coherent and incoherent energy transport is discussed for several initial energy distributions. Finally, we discuss for specific examples the influence of the deviations from the ideal structure.

# Photoswitchable molecular and supra-molecular receptors

Michael Alfimov

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In this report will be present examples the controlling spectroscopic and photochemical properties of molecules trough molecular organization by intermolecular interaction.

Host-guest complexes  $\beta$ - cyclodextrin with organic molecules and nanostructures of host-guest complexes demonstrate strong change fluorescence and photofluorescence spectra aromatic molecules through molecular organization at room temperature. Nanostructures of host-guest complexes of cyclodextrines possess bright phosphorescence with well defined vibronic structure, but free aromatic molecules in liquid solvent do not exhibit phosphorescence at room temperature.

Another example of the influence of molecular organization on fluorescence is the properties of novel class crown containing dyes which can work as photoswitchable molecular receptors.

The dyes are highly sensitive to metal cations and exhibit hypsochromic shifts of absorption and fluorescence bands. The design of crown containing dyes can be used to influence the stability and structure of the complexes formed between dyes and metal cations. Supramolecular complexes consisting of inclusion (1 ligand : 1 cation), sandwich (2 ligand : 1 cations) and dimeric (2 ligand : 2 cations) supramolecular complexes, have been found for different types of dyes.

Via complexation crown containing dyes with metal cations and self organization of complexes, spectroscopic and fluorescence properties of the dyes change, mainly decrease of lifetime (10 - 100 times) or increase of the intensity of electronic transition (extinction coefficient, life time etc.).

# Molecules with Moving Parts : Hydrogen Bond-Assembled Molecular Machinery

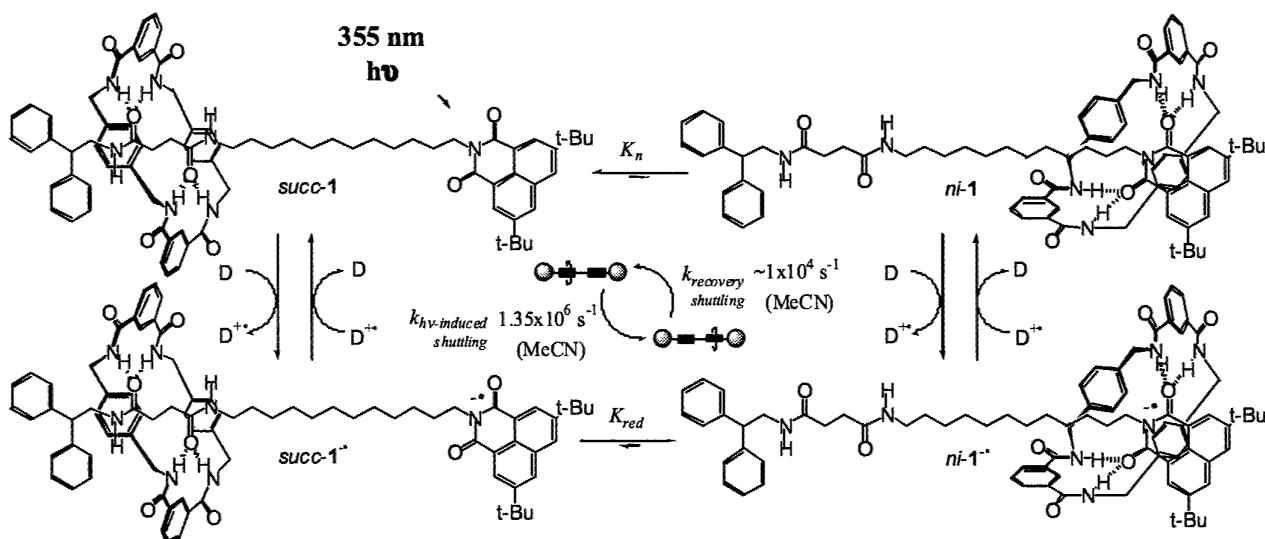
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Mechanically-interlocked molecules (catenanes and rotaxanes) are increasingly attracting attention because their architectures offer properties and opportunities for exploitation not available to conventional materials.[1] Hydrogen bond-directed assembly, in particular, offers powerful strategies for the synthesis of such structures on a scale where practical applications become a realistic area for study.[2-10].

Here we discuss both simple and complex molecules-with-moving-parts (*e.g.* 1); beginning with their synthesis and unusual properties and featuring their evolution into photonic molecular 'machines'.

A hydrogen bonded, light-fueled, translational molecular motor.



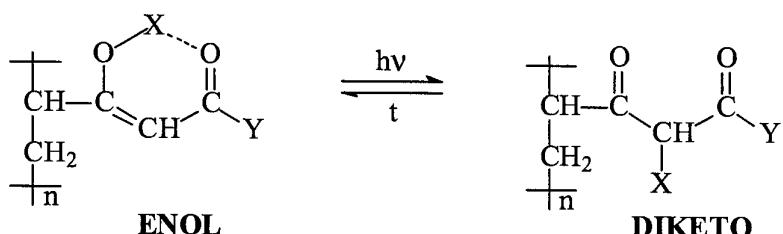
- [1] "Molecular Machines" special issue, *Acc. Chem. Res.* **34**, 409 (2001).
- [2] W Clegg, C Gimenez-Saiz, D A Leigh, A Murphy, A M Z Slawin, S J Teat, *J. Am. Chem. Soc.* **121**, 4124 (1999).
- [3] M S Deleuze, D A Leigh, F Zerbetto, *J. Am. Chem. Soc.* **121**, 2364 (1999).
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- [5] D A Leigh, A Troisi, and F Zerbetto, *Angew. Chem. Int. Ed.* **39**, 350 (2000).
- [6] V Bermudez, N Capron, T Gase, F G Gatti, F Kajzar, D A Leigh, F Zerbetto, S Zhang, *Nature*, **406**, 608 (2000).
- [7] A M Brouwer, C Frochot, F G Gatti, D A. Leigh, L Mottier, F Paolucci, S Roffia and G W H Wurpel, *Science* **291**, 2124 (2001).
- [8] G W H Wurpel, A M Brouwer, I H M van Stokkum, A Farran and D A Leigh, *J. Am. Chem. Soc.* **123**, 11327 (2001).
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- [10] M Asakawa, G Brancato, M Fanti, D A Leigh, T Shimizu, A M Z Slawin, J K Y Wong, F Zerbetto and S Zhang *J. Am. Chem. Soc.*, asap contents 1<sup>st</sup> March 2002.

# Polymeric $\beta$ -dicarbonyl Compounds as Structural Basis for Intelligent Systems with Multifunctional Nature

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In general, the development of new materials for application in **high-tech** technologies first of all will involve the design and synthesis of molecules which possess the aforementioned properties, followed by incorporating these compounds into supramolecular assemblies, in order to obtain ordered molecular systems. New, rich possibilities give combination **polymeric  $\beta$ -dicarbonyls /sensitive organic compounds**. The polymeric  $\beta$ -dicarbonyl part possesses keto-enol tautomerism. The equilibrium can be shifted under the influence of different actions. The process is very simple - transfer of H atom into the molecule.



The structure of the polymer  $\beta$ -dicarbonyl part can be modified in different functions. The transfer between the tautomeric forms is reversible and can be realized many times. The combination of these structural characteristics and the multifunctional properties of the functional parts, connected with the  $\beta$ -dicarbonyl part can be base of the development of the sensitive multifunctional systems.

In such systems can be realized several depending and independent processes :

1. **Processes connected with the basis- polymeric chain:** a/ *photoinduced proton or groups, cations, anions* transfer (keto-enol, enamin-ketimin, thiol-thione, enhydrazine-hydrazone, acylotropic-, cationotropic-, anionotropic tautomerism). b/ *photoinduced metallotropic tautomerism* (photoinduced isomerization, pyrazolone derivatives).

2. **Processes connected with the sensitive parts:** cis-trans-, valence-, open-closed-isomerization, electrochemical oxidation and reduction, photochemical synthesis of dyes, photo-, electro-, thermo-, halo-, radio-, piezochromism, conductivity.

3. **Mixed processes – combination on the basis of antenna effect in the polymer systems.**

The experimental and theoretical data on the molecular reorientation and interaction under the radiation in various systems containing light absorbing chromophores showed that the most important factors, which control the phenomenon are chemical changes and the photoselection of the chromophores. Even in diluted solutions, they provide, respectively, the necessary rotational mobility of the chromophores and the consequent optical anisotropy of medium. In condensed phases (LB films, polymers, host-guest systems, sol-gel materials) the shape of the intermolecular interaction potential is also of paramount importance.

The multifunctional polymer systems, based on recent advances in new organic sensitive materials will beyond doubt play a key role in future (nano)-technology developments. These systems, with independent and different sensing, processing, and actuating functions, enhance performance capabilities. Such material systems are said to be '**Intelligent**'.

# Quantum Chemical First Principles Design of Single Supermolecule Photoactive Machines and Molecular Classical and Quantum Logic Devices

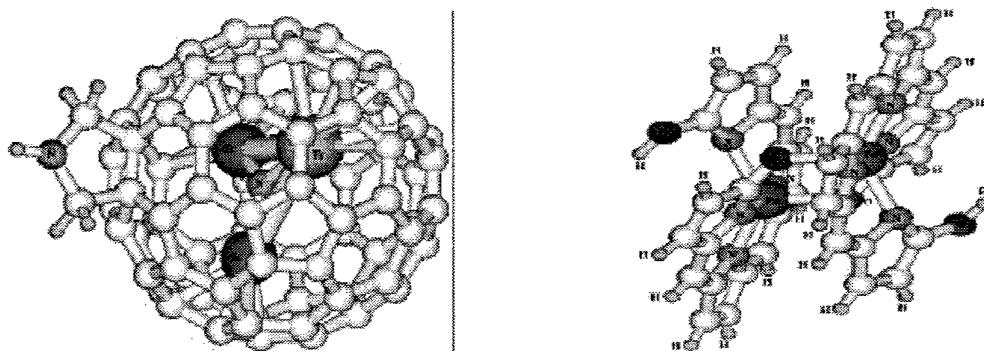
Arvydas Tamulis<sup>a</sup>, Jelena Tamuliene<sup>a</sup>, Zilvinas Rinkevicius<sup>b</sup>, Vykintas Tamulis<sup>a,c</sup>

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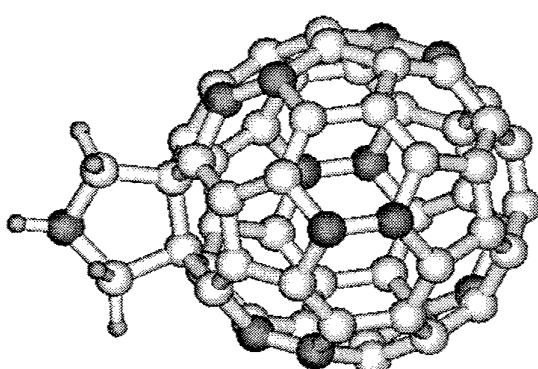
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Quantum mechanically *ab initio* and DFT-Time Dependent designed light-driven, single supermolecular devices based on fullerene, biliverdin and photoactive molecules and supermolecules could form the basis for logically-controlled organic molecular machines and molecular classical and quantum computers. Organic and organometallic molecular computers have advances in nano-size and pico- or even femto-second speed as well as of in



principle new quantum computation compared with conventional silicon-based chips.

Theoretical molecular physics can provide the basic understanding needed to design such a single supermolecule devices by calculating the optimized geometries, quantum state energies, electron and proton charge transfer, NMR, EPR, etc. of candidate molecules and suggesting new supermolecules molecules with the desired quantum properties. Using advanced computational physics tools we, for instance, elucidated the energies and pathways of optically-induced charge transfer and the *trans-cis* isomerization of azo-dyes based supermolecules, and the electrical and magnetic properties of a fullerene ( $\text{ErSc}_2\text{N}@\text{[CH}_2\text{CH}_2\text{NH]C}_{80}$ , figure on left), biliverdin (figure on right) derivatives and azofullerene derivatives (figure in the bottom). A molecular logic gate of classical digital molecular machine would change its quantum state in response to optical signal and pass the emitted electron via chip doing simultaneously *trans-cis* isomerization that predict motion. Set of gates of classical digital molecular computers are designed based on light driven charge transfer in fullerene-containing supermolecules. Designed basic elements of quantum computers are based on proton NMR calculations in biliverdin derivatives that generate up to eleven quantum bits (figure on right), EPR estimations in endohedral fullerenes (figure on left) possessing up to six QuBits for quantum computation and nitrogen atom NMR in azo-fullerene  $\text{CH}_2\text{CH}_2\text{NHC}_{48}\text{N}_{12}$  derivatives (figure in the bottom) generating up to twelve QuBits.



It were designed various biologically active, fluorescing, small-gap semiconductor and proton-transfer switching single supermolecular devices based on biliverdin, fluorescein, CdS organic and white phosphorus organo-metallic complexes.

## STM-induced photon emission

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The tunneling of electrons between the tip of a scanning tunneling microscope (STM) and a sample is accompanied by the emission of photons. This luminescence phenomenon can be used to study local radiative processes at surfaces by combining the high spatial resolution of the STM and optical techniques. In this way, spatial maps of photon intensity modulations can be measured with lateral resolutions of less than 1 nm. We discuss the basic concepts of STM induced light emission and present results from quantum well systems and adsorbed molecules.

# STM-induced light emission from single-nanoparticles and molecules

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Several experimental techniques have been developed to break the diffraction barrier in order to analyze and even control photonic properties of matter at subwavelength resolution. For biases larger than  $\sim 1V$ , the tunnel junction of a Scanning Tunneling Microscope can behave as a nanoscale light source. The analysis of the light emitted by a STM thus permits local photonic studies with higher resolution than near-field optical methods. However, the observed contrasts can have several optical or electronic origins.

We have analyzed STM-induced light emission from a from hybrid organic metal nanoscale self-assembled systems based on silver nanoparticles surrounded by alkane molecules. We have thus evidenced the influence of frequency-depended local plasmon modes.[1] Moreover, taking advantage of (1) the site-dependence of the STM luminescence efficiency of individual nanoparticles [2] and (2) the ability to manipulate a single particle between two adjacent sites through interaction with STM tip, we have realized a tip-controlled switching of the luminescence of a single 4-nm alkane-thiol covered nanoparticle [3].

In contrast with extended luminescent systems, the highly local nature of this light source makes possible the existence of strong time correlations between successively emitted photons. Such correlations provides informations on the local mechanisms and dynamics of luminescence processes. We have applied time-autocorrelated two-photon counting measurements to STM-induced light emission, with time resolutions down to the nanosecond range. We thus observed a strongly bias-dependent bunching phenomenon.[4] The spatial dependence of this effect offers new contrast mechanism for imaging photonic properties at surfaces.

STM tip-controlled local luminescence and time correlation analysis can be expected to improve our understanding of photonic phenomena at the nanoscale. We will discuss the application of these techniques to molecular systems.

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# Optical Properties of Ultrathin Epitaxial Films of PTCDA on Au(111)

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Research activity on molecular solids has gathered pace in recent years as these materials have a wide range of interesting properties, emerging industrial interest with real applications at the horizon, and possible future applications that will enable electronics to move into the nanoscale. Indeed, several organic based semiconductor devices, such as light emitting diodes, transistors, photovoltaic cells, etc., have been recently demonstrated to have very interesting characteristics, in some cases comparable or even superior to those of their inorganic counterparts.

Over the last few years research on molecular crystals has demonstrated that high quality samples, precise structural data, and a detailed understanding of the physical properties is essential, with special emphasis on thin films and interfaces. In this respect, the use of highly controlled growth techniques like *Organic Molecular Beam Epitaxy* (OMBE) is becoming more and more important, aiming at high quality thin films with controlled crystal structure and morphology, therefore displaying well defined physical properties.

In our contribution we will discuss the special optical properties of ultrathin films of an archetypal organic material, namely PTCDA (perylene-3,4,9,10-tetracarboxylic-3,4,9,10-dianhydride). Highly ordered organic thin films on a gold single crystal have been prepared by means of OMBe with submonolayer to multilayer coverage. All films were structurally characterized by combining Scanning Tunneling Microscopy (STM) with Low Energy Electron Diffraction (LEED), clearly indicating epitaxial growth in the point-on-line mode.

Differential Reflection Spectroscopy (DRS, a variant of reflection absorption spectroscopy) both *ex situ* and *in situ* has been applied to measure the optical characteristics of those films. The results clearly show that ultrathin layers have different optical properties as compared to thicker films, which in turn match the results known for long from polycrystalline samples. The results are further compared to thin films grown on mica.

# Scanning Tunneling Microscopy of Long Chain Organic Molecules at the Liquid/Solid Interface

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Self-assembled monolayers (SAMs) of organic molecules currently attract considerable attention because of their potential applications in bio and chemical sensing, corrosion inhibition, wetting control and electronic devices. The imaging of organic molecules physisorbed at the liquid-solid interface has provided a particularly fruitful area of investigation for scanning tunneling microscopy (STM). On the one hand, this kind of studies can elucidate the nature of the interactions between the surface and the adsorbate, but also the role of the underlying structure of the surface in the determination of an organized arrangement of molecules. On the other hand, STM can provide precise information concerning the tunneling mechanism through molecules.

We report on a systematic structural STM investigation of the two-dimensional supramolecular organization of different organic structures. Normal alkanes, long chain molecules terminated by trimethylsilyl groups, thiols and fullerene were imaged on reconstructed Au(111) surfaces at the liquid/solid interface. The observed structures are discussed in terms of commensurability and of competition between the molecule-substrate and the molecule-molecule interactions. The proposed models are in good agreement with the results we obtained.

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## Electronics, fluidics, and biology: new horizons and opportunities for Nanoscale optics.

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The Center for Electron Transport in Molecular Nanostructures at Columbia University is one of six Nanoscale Science and Engineering Centers (NSEC) created by the NSF. The Nanocenter Team involves 16 members of Columbia University faculty with active collaborations with research programs at Lucent Technologies and with IBM Research. This team represents a unique assembly of capabilities in chemical synthesis and chemical manipulation, in fundamental physics of electron dynamics, and in nanoscale device fabrication and characterization. The primary goal of the Columbia Nanocenter is to bring a new level of fundamental understanding to the fascinating and technologically important phenomena of electron transport from an electron “source” (for example a metal at a defined electric potential) to a “drain” (for example a metal maintained at ground potential) through a single molecule or through molecules assembled on a nanometer scale. Thus we are developing a detailed understanding of the growth and structure of nanoscale assemblies of molecules that exhibit two-dimensional electron transport phenomena such as pentacene. A second set of activities centers on chemical modification and chemical control of carbon nanotube transport properties. A third set of activities involves explicit exploration of conductance in individual molecules, including synthesis of molecules that can be chemically bonded to metals, construction of nanoscale electrode structures or “molecular sockets”, contact of individual molecules to these sockets, measurement of electron conductance phenomena of single molecules bound to defined electrode structures, and theoretical understanding of these systems. We will review this program and explore opportunities in nanophotonics that may be created as a result.

As one example of the opportunities forged through nanoscale fabrication, for example, we have begun to explore the construction of fluidic devices on a micrometer and nanometer scale and the optical characterization of flow properties within these structures. We have fabricated fluidic devices based on polymeric structures and we have examined the control of flow within these channels both experimentally and theoretically. In particular we have developed structures that allow for the controlled mixing of reagents within these channels. We will describe these structures and the resulting flow characterization.

Nanotechnology offers many opportunities for optical exploration of fundamental processes in biological systems. In one example, we have fabricated in artificial structures in polymeric materials designed to simulate a pore or “lacuna” found in common bone structures that contain living cells such as osteoblasts. We have also fabricated structures that allow us to simulate the nanoscale canal or canaliculus that interconnects these pores. Through the use of microfluidic flow, we can control the environment of the cells and thus in principle we can monitor the cell behavior optically. We have demonstrated that we can isolate osteoblast cells within these structures. This system demonstrates the capability to simulate the environment of a cell in a form that allows for the direct optical examination of the response of these cells to changes in environment. We will speculate on potential applications.

# Highly efficient two-photon absorbing dendritic molecules

Kwang-Sup Lee

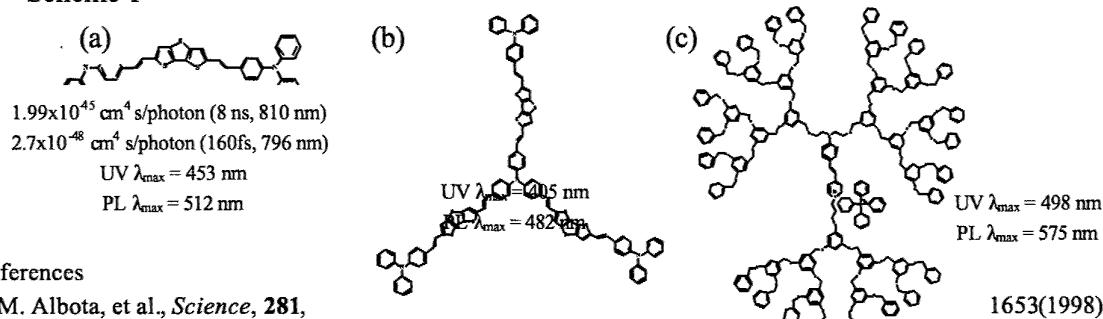
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Nonlinear optical organic materials exhibiting large two-photon absorption (TPA) behavior have drawn interest in recent years owing to the fact that it occurs under the irradiation of sufficiently high intensity of low energy photons. TPA materials with a large cross section ( $\sigma$ ) can be utilized for various applications such as for two-photon-excited fluorescence microscopy, optical power limiting, three-dimensional optical data storage, photodynamic therapy and two-photon induced biological caging studies.

Recent reports from two different groups [1,2] disclosed their design strategies for efficient TPA molecules by a systematic investigation of chromophores with various electron-donor (D) and electron-acceptor (A) moieties, which are attached symmetrically or asymmetrically to a conjugated linker ( $\pi$ -center); D- $\pi$ -D, A- $\pi$ -A or D- $\pi$ -A. The typical difference in their approaches is that one deals with *trans*-stilbene as  $\pi$ -center with various D/A pairs, and the other does with chromophores bearing fluorene as  $\pi$ -center, which is asymmetrically coupled with D and A; D- $\pi$ -A. While the former emphasizes the importance of conjugation length, D/A strength and molecular asymmetry, the latter stresses planarity of fluorene as  $\pi$ -center. Based on both molecular design concepts we prepared various new TPA molecules having fluorene, dithienothiophene (DTT) and ethynylenephenylene units as  $\pi$ -center. Among them, DTT-based molecules showed highest TPA activities (Scheme 1a) [3]. This result indicates that the planarity of  $\pi$ -center might be more crucial molecular factors than structural symmetry and donor strength.

To expand the utility of TPA materials, the enhancement of TPA activity by the increase of the chromophore number density is required. For this purpose, dendrimers with conjugated chain branches (see Scheme 1b) have been synthesized. In addition, most two-photon absorption (TPA) compounds based on  $\pi$ -conjugated double bond presented a problem of reduction in TPA activities due to the quenching of fluorescences resulting from the formation of  $\pi$ -complex by the chromophore-chromophore interaction. This occurs both in solid state and in solutions of high chromophore concentrations. To prevent the interaction with other chromophores in vicinity, we prepared TPA dendrimers (see Scheme 1c) by attaching Frechet-type dendron on TPA chromophore center. The detailed results related with TPA activities including optical power limiting behavior on various organics and dendrimers are presented in this paper.

Scheme 1



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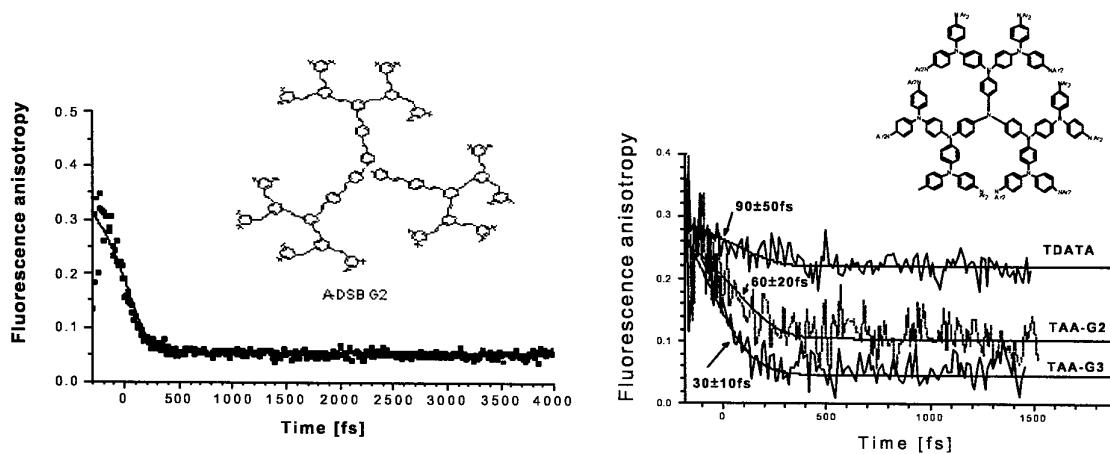
# Investigation of Optical excitations in Novel Dendrimers Using Ultra Fast Anisotropy Measurements.

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Dendrimers have shown great potential for applications in areas such as light harvesting, light emitting devices, as well as medicine. The search for a model that can be used to describe the migration of optical excitations in homogeneous dendrimers has attracted great attention. In most cases in a organic dendrimer the conjugation is disrupted at the branching point, however the excitation may be delocalized. The strength of interactions among neighboring chromophores plays a key role in determining the energy migration mechanism. Conversely, having many identical chromophores held tightly together in an ordered macromolecular architecture will allow for many dipoles to be accessible for optical excitation. Therefore, the relative orientation of dipoles will be important in determining the mechanism of energy migration. In our dendrimer systems (as seen below) a collection of oriented dipoles are excited by polarized light, and the distribution of the optical excitation among the dipoles leads to depolarization of the emission. Through our investigation we have found that the anisotropy measurement is a very powerful tool for investigating energy migration in such branched dendritic architectures.

We investigated excitation migration dynamics in dendrimers in which nitrogen is at the branching point. The energy migration processes in the dendrimers were investigated utilizing ultra fast time resolved fluorescence anisotropy measurement. We have evidence that in some cases these dendrimer systems can have very strongly inter-acting branching groups as illustrated by the fluorescence anisotropy decay to a residual value within  $\sim 100$  fs. This fluorescence anisotropy decay showed strong dependence on generation number in the case for the triarylamine type dendrimer seen below. This fast energy depolarization is discussed through a coherent excitonic mechanism among dipoles oriented in different directions. We believe the formation of coherent domains leads to a fast energy redistribution over a large portion of the dendrimer macromolecule.



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# New Organic Dendrimers with Greatly Enhanced Multi-Photon Absorption for Photonics Applications

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Tree-like dendritic structures based on identical repeat units and a variety of branching patterns are an exciting new class of materials with a myriad of potential applications at the nanophotonics level. Dendrimers offer advantages over traditional linear polymers containing a mixture of chain lengths in that they are monodisperse macromolecules amenable to detailed structure-property relationship studies. For the study of multi-photon absorption (MPA), dendrimers can be designed using chromophore repeat units with known photonic properties, and the resulting highly branched three-dimensional structures allow a very high packing density per unit volume, with the number of chromophore repeat units increasing exponentially with dendrimer generation.

G-0, G-1 and G-2 generations of a 4-arm branched dendritic bis-(diphenylamino)stilbene have been synthesized in modified form that incorporates n-butylthio substituents (SBu) in the para positions of each phenyl ring. Thus the G-0 4-arm dendrimer contains 8 SBu groups, the G-1 dendrimer 16 SBu groups and the G2 dendrimer 32 SBu groups. The respective molecular weights of the three dendrimers are: G-0 (2,997), G-1 (5,157 and G-2 (10,878). We have recently shown that these new dendritic materials have extremely large intrinsic two-photon cross-sections for 100 fs laser pulses. The TPA maximum for the dendrimers is clearly red-shifted with respect to bi-(diphenylamino)stilbene (DPAS), as well as the linear absorption. It is interesting to note that the lowest estimate for  $\sigma_2$  in the G-0 dendrimer is 8 times higher than that of DPAS, whereas the number of stilbene repeat units is only five times higher. For the largest dendrimer we have made to date (G-2), the intrinsic cross-section of 11,000 GM units is, to our knowledge, the highest intrinsic value for a monodisperse macromolecule. Most recently we have measured the three-photon spectra for this same dendrimer series, and found both large MPA, and that the three-photon absorption transitions coincide in energy with corresponding linear transitions. This suggests different spatial localization of fluorescing and dark (excitonic) states.

We will also report the first comprehensive structure-property study of the effect of the repeat unit identity (e.g. stilbene versus PPV-dimer) on the magnitude of TPA in 4-arm dendrimer structures. Such studies are extremely important for the rational design of new dendrimers with even larger MPA.

# Dendritic Polymers for Optical Applications

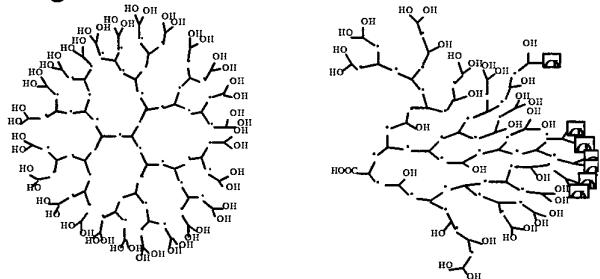
Anders Hult

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There is significant interest for polymers in electronics and/or opto-electronics. This is due to the fact that polymeric materials are relatively easy to give certain properties. From a processing point of view polymers are also advantageous over inorganic materials.

Dendritic macromolecules (dendrimers<sup>1</sup> and hyperbranched polymers<sup>2</sup>) are synthesized from  $AB_x$ -type monomers (where  $x$  is two or greater) resulting in macromolecules with a highly branched architecture and a multitude of end-groups (figure 1). Dendrimers are symmetrically branched structures while hyperbranched polymers are irregularly branched. Both types have a multitude of end groups.

The field of dendritic polymers is still rather young and unexplored. Many groups worldwide work on the synthesis of macromolecules having a highly branched architecture. However, not many focus on dendritic polymers as a *material* – most groups deal with pure synthetic challenges.



**Figure 1**

*Schematic representation of a hydroxy-functional dendrimer (left) and a hydroxy-functional hyperbranched polymer (right).*

This paper will present the use of functional dendritic polymers to build complex materials for use in photonic devices. The controlled shape, size and differentiated functionality as well as their ability to form isotropic and anisotropic assemblies, compatibility with many other types of nanometer scale building blocks (DNA etc), their potential for self-assembly, their capacity to form surfaces and interfaces and their ability to either encapsulate or be engineered into unimolecular devices make dendrimers uniquely versatile amongst existing nanometer scale building blocks.

We have demonstrated that fluorinated hyperbranched polymers are potentially useful for optical waveguide applications. The amorphous structure and its low C-H bond content lead to very low losses in the NIR, 0.1 dB/cm at 1550 nm. The multiple end-groups inherent to the hyperbranched architecture allow drastic changes of the initial refractive index.

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# Optical Excitations in Novel Dendritic Architectures

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The branched architecture affords many interesting properties that are different from those of their linear analogs. Organic dendrimers have shown great promise in many applications such as nonlinear optics, organic light emitting diodes, as well as light harvesting. However, the mechanism of intramolecular energy transport in dendrimers and other branched systems is not well understood. There is also a limited level of understanding for the optical excitations in a new architecture involving dendrimers and metal nanoparticles, which are called dendrimer-metal nanocomposites. Dendrimer nanocomposites are a new class of materials and it has been found that the organic dendrimer component may act as either a host or a scaffolding macromolecule for the metal particles in this novel architecture.

In this contribution we present the time-resolved fluorescence of conjugated dendrimers with femtosecond time resolution. The excited state relaxation of a nitrogen-cored distyrylbenzene-stilbene (A-DSB) dendrimers was investigated by polarized fluorescence upconversion spectroscopy. Energy transfer processes from the dendrons to the core can be described by a Förster mechanism (hopping dynamics) while the inter-branch interaction in A-DSB-core was found to be very strong indicating the crossover to exciton dynamics. The properties of small branched molecules with high degree of symmetry are also of interest in many research areas. Measurements of ultra-fast fluorescence anisotropy decay in model branched dendritic molecules of different symmetry are reported in this contribution. These molecules contain the fundamental branching center units of larger dendrimer macromolecules with either three ( $C_3$ ) or four ( $T_d$ , tetrahedral) fold symmetry. The anisotropy dynamics for a adamantane-centered tetrahedral system (decay time 880fs) can be qualitatively explained by Förster-type incoherent energy migration between adjacent chromophores. For a nitrogen-centered trimer system the fluorescence anisotropy decay time (35 fs) is found to be much shorter than that of the tetramers and the decay cannot be attributed to an incoherent hopping mechanism. In this case a coherent inter-chromophore energy transport mechanism should be considered. Time-resolved fluorescence measurements for nitrogen-centered donor-acceptor molecule of  $C_3$ -symmetry revealed the existence of short-lived (35fs) intermediate symmetrical excited state, which evolves to localized charge transfer state of lower symmetry  $C_2$ . This is an important issue in understanding of the mechanisms and time scales of the optical nonlinearities associated with this structure.

In this contribution we also discuss the fluorescent and nonlinear properties of metal-dendrimer nanocomposites. The ultrafast emission is reported in novel transition metal-dendrimer nanocomposites. Fluorescence dynamics have been investigated in nano-scale particles of different geometries. For dendrimer nanocomposites as well as for both gold nanorods and nanospheres an ultra-fast fluorescence decay component was observed on the order of ~100fs. The spectra of the fast emission have also been measured. The origin of the emission and the mechanism the ultrafast emission decay will be discussed.

# Challenges in Nanostructured Organic Electronic Devices

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The past 20 years have seen the rapid development of the science and technology of organic semiconductor devices for applications in electronics and optics. Following the seminal contributions of Tang[1,2] and VanSlyke[2] in the demonstration of high efficiency organic electroluminescence and solar energy conversion, we are now entering a period when organic electronics is finding a permanent place in the field of practical devices; most notably as flat panel displays.

Yet many unanswered questions about the physics and chemistry of the vast range of organic semiconductors remain, and many challenges must still be faced before further widespread application of these materials can occur.

In this talk I will focus on some of the most significant challenges that lie ahead. In particular, I will concentrate on the following topics:

1. The limits and methods for achieving very high performance organic light emitters, photodetectors, transistors and other electronic devices.
2. The limits to the control of structure and fabrication at the nanometer scales necessary for achieving high performance organic devices. In particular, such new patterning technologies such as organic vapor phase growth through small apertures[3] and direct contact formation through stamping of the metal contacts[4] will be discussed.

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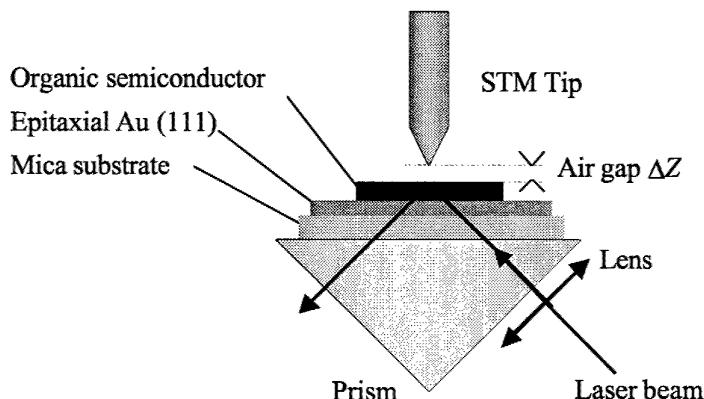
# Laser-Assisted Scanning Tunneling Spectroscopy: a new tool to probe local photocarriers in organic semiconductors.

Denis Fichou, Fabrice Charra, Nathalie Katsonis, and Oleksandr Marchenko

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Photo-induced charge transport in organic semiconductors strongly depends on the degree of molecular and crystalline ordering. But most studies have been performed on macroscopic dimensions leading to overall parameters. In order to reach the intrinsic behavior of highly organized materials, it is necessary to access defect-free nano-domains with the possibility not only to image them but also to submit them to electrical and optical excitations.

The metallic tip of a scanning tunneling microscope (STM) can be used as a through-space nano-contact to a semiconductor sample. Tunnel current-voltage (I/V) and current-tip height (I/Z) curves can be recorded for each point of the scanned area with the possibility to reach molecular resolution. Direct correlations between the local morphology and its electrical behavior can thus be established.



The influence of light is then investigated by coupling the organic nano-junction to a laser beam through a prism in a pure optical way, thus reducing greatly thermal effects [1]. Monitoring the tip-sample distance at the angström level allows to tune the I-V characteristics of these organic tunnel nano-junctions. Beside continuous lasers, we have also used a femtosecond pulsed laser which provides multiphotonic excitation and the possibility to add time resolution to spatial resolution [2]. We report here on recent results obtained with various organic molecular semiconductors (pentacene, etc) and C<sub>60</sub>-polymer blends and show that laser-assisted tunneling spectroscopy provides a powerful tool to study the physics of local photocarriers.

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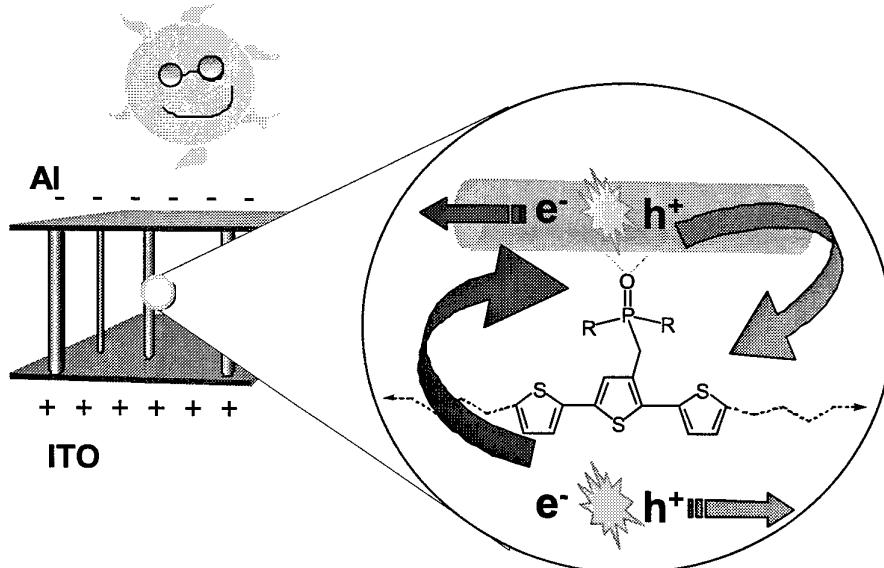
# Organic-Inorganic Nanocomposites for Solar Cell Devices

Claire Pitois, Delia J. Milliron, Jean M. J. Fréchet and Paul Alivisatos

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Semiconductor nanoparticles have been integrated with organic semiconductors in optoelectronic devices to take advantage of their complementary properties [1,2]. Solar cells with an organic-inorganic composite active layer have been demonstrated using soluble semiconductor nanocrystals (Cd/Se) and conjugated polymers (3-hexyl polythiophene) [3]. Such hybrid devices can combine the optical advantages of inorganic semiconductors with the flexibility and processibility of polymers. However, the extent to which these properties can be exploited depends critically on the control of the interface between these dissimilar materials.

To control this interface electroactive surfactants have been synthesized to specifically bind to the nanoparticles. The resulting nanoparticle-surfactant complexes are the building blocks to assemble an optimal hybrid solar cell. Here we demonstrate the direct attachment of oligothiophene surfactants to semiconductor nanocrystals. The resulting composite material absorbs over a broad range of the solar spectrum and yields efficient charge transfer between the organic and the inorganic components. These complexes can then be incorporated into solar cells to take advantage of charge transfer to generate current.



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## Electronic properties and the Magnetic Behaviour of Hybride Organic-Inorganic Advanced Materials

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In the past decade several metal-containing liquid crystal(LC) polymers have been prepared and characterized<sup>1</sup> . Liquid crystals with transition-metal core groups ( metallo-mesogens ) are increasingly a topic of investigation since metals can impart usefull shapes and properties which are not easily produced in totally organic liquid crystals<sup>2</sup> .A major distinction between metallomesogens and most organic mesogens is their greater tendency to exhibit intermolecular dative coordination bonds in the solid state<sup>2</sup> .These interactions also provide an opportunity to create usefull supermolecular organizations ,with non-centrosymmetric asemblies with second order nonlinear optical<sup>3</sup> and ferroelectric properties<sup>3,4</sup>.

The development of electronic devices and sensor techniques requires continuously new materials to cope with the increasing demands. A promising family of materials for this type of developments is that of  $[M_xL_pL_q]_n$  where M is a metallic cation (eg.Fe(II),Fe(III),Co(II),Co(III),Cr(III),Cu(II),VO(IV),or lanthanide Ln(III) as Er(III),Tb(III),Eu(III) ) and L ,L are organic ligands one of them possesses the indispensable property of polymerization always with other comonomers.Using as comonomers vynil acetate ,styrene or methyl methacrylate we can modify the physico-chemical properties of the old classic polymers<sup>5</sup> .These molecules are of the push-pull type where the mobility of electrons is ensured by the coordination bonds Ligand-Metal/Donor-Acceptor where the so called  $\pi$  - d interactions are present<sup>6</sup> .The contribution will present results of the electronic and magnetic properties of these molecular architetures.The practical importance of these kind of materials will be also discussed.

**Acknowledgments** :This work was supported by the Grant of the Ministry of Education A/424/2000-2002.

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# Nanoprecise Self-Assembly of Electro-Optic and Electroluminescent Molecular Arrays

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Self-limiting chemisorptive siloxane condensation chemistry offers the attractive possibility of constructing, with monolayer precision, robust, conformally adherent, optically functional, interlinked assemblies composed of designed, microstructurally and photophysically well-defined building blocks.

We discuss here the implementation of such strategies for the fabrication and soft lithographic patterning of organic electro-optic and emissive structures.

In the electro-optic area, we report:

- i) efficient, automatable routes to very large electro-optic response self-assembled superlattices,
- ii) a new way to tune the refractive indices of such materials,
- iii) the fabrication and properties of the first self-assembled electro-optic light modulator.

In the light-emitting diode area, we report:

- i) electrode passivation and charge injection balance control,
- ii) elucidation of matrix order vs. disorder effects on charge transport,
- iii) interfacial electrode-organic cohesion effects on injection efficiency and device robustness,
- iv) the fabrication of emissive nanodiodes having dimensions less than 50 nm,
- v) superior device characteristics of high-work function anode alternatives to ITO.

# Aggregation Control of Fluorescent Dyes in Mesoscopic Dome Structures

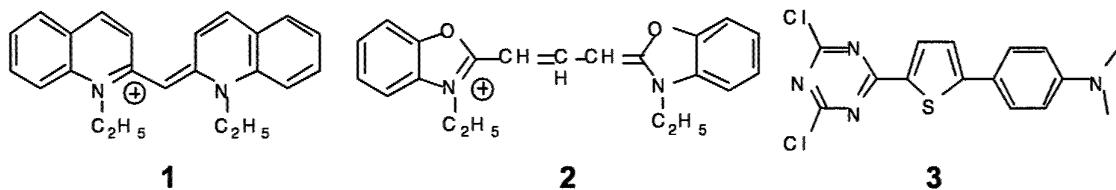
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1) Chitose Institute of Science and Technology, Faculty of Photonics Science, Hokkaido, Japan

2) JST, PRESTO

The aggregation state and the nanoscale structure of organic materials plays an important role for the function of many photonics devices. OLED devices often depend on the amorphous state of the emitting material, whereas for non-linear optical applications a crystalline form of the functional material is desired. Thus great efforts have to be made to ensure the desired aggregation form of the photonic material is achieved and maintained over the lifetime of the device.

Here we report that it is possible to control the aggregation state by patterning the photonic material into micrometer-sized "domes". Recently it was reported that by casting a dilute polymer solution onto a substrate, a dewetting-induced formation of micrometer-sized polymer domes or lines can lead to regular 2-D patterns of polymers [1]. Here, we describe the use of micronsized polymer domes for the formation of nanoscale aggregates and nanocrystals of organic dyes, like 1-3.

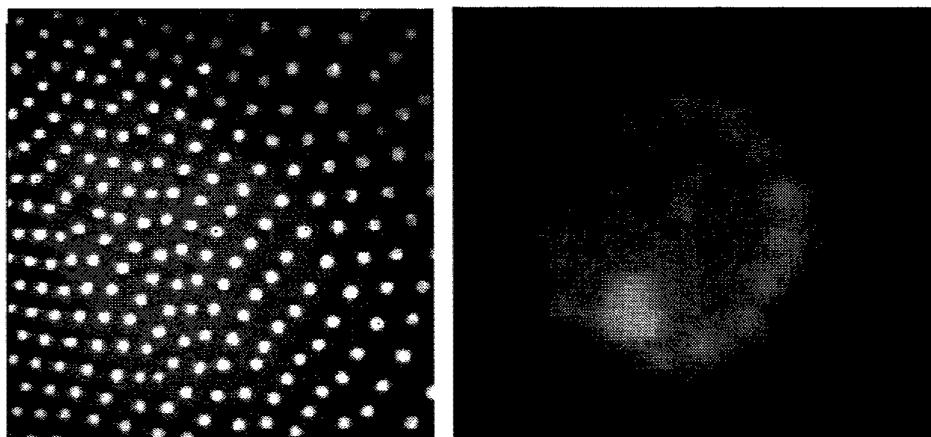


1

2

3

Aggregation is determined by the interplay between two entirely different processes during solvent evaporation: dewetting-induced dome formation, which is a process **far from** equilibrium, and aggregation, which is a process **towards** equilibrium.



As a result, various patterns of dye aggregates in polymer microdomes can be created, including hierarchical patterns with circular dye aggregates within each dome, as can be seen in the fluorescence micrographs.

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# Intercalation of Rhodamine B in Molybdenum Disulfide

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The insertion of chemical species into low-dimensional solids often leads to behaviours differing from those observed in the solid state. Thus, some semiconductors or other luminescent compounds inserted in zeolites or in micelles display features, which are nearer to that of the isolated and or confined species rather than to the pristine solids. Self assembling features, like the formation of tri- and tetrานuclear lithium/amine clusters of ca. 6 Å diameter we had observed in the co-intercalation of lithium and amines into molybdenum disulfide, could also influence the optical properties of intercalated species

In this paper we describe the preparation of solids formed by the insertion of rhodamine B (RB) in lamellar structures, specifically in molybdenum disulfide, both pure and modified MoS<sub>2</sub> by the intercalation of octadecilamine (ODA). That in order to explorer the functionality of improving light emitting structures by enhancing the spatial and chemical control of the location of the emitting species.

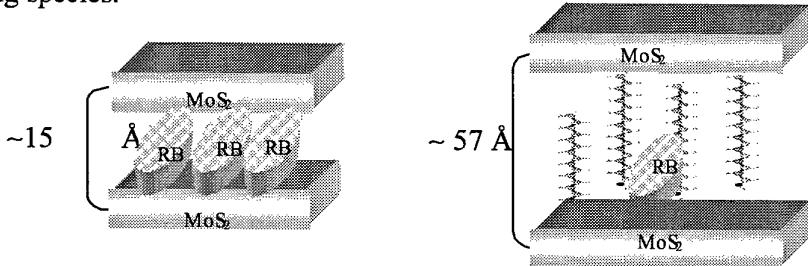


Figure: Scheme of intercalates MoS<sub>2</sub>/RB and MoS<sub>2</sub>/ODA/RB. Interlaminar distances in Å.

The insertion reaction and characterisation of the products is performed following typical methods used for the intercalation in MoS<sub>2</sub>. Luminescence spectra under blue laser (457.9 nm) excitation of rhodamine B crystals show a broad band centred at 700 nm, far from the characteristic emission of this dye in solution (ca. 500 nm). However, intercalated products Li<sub>x</sub>MoS<sub>2</sub>/RB and Li<sub>x</sub>MoS<sub>2</sub>/ODA/RB (x<0.1) show emission bands centred at about 620 nm and 580 nm, respectively.

These results are compared with features observed for this dye in solution and adsorbed in other solids and discussed considering intermolecular interactions, confinement, as well as eventual surface and matrix effects.

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# Nonlinear-Optical Properties of Self-Assembled Molecular J-Aggregates of Pseudoisocyanine in Nanometer Films

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J-aggregates are well-known for their unique optical properties and high optical nonlinearities. The nonlinear-optical properties of organic dye J-aggregates has been intensively studied for application in the future optical telecommunication and signal processing systems with ultrahigh bit rates (Tbit/s) [1]. Thus novel photonic materials should combine a large magnitude of the nonlinear optical response (intensity dependent refractive index and absorption) with a high speed of the nonlinear phenomenon (less than 1 ps) and in addition, important requirements are thermal and photochemical stability, and a high optical quality.

It was shown [2] that the long-alkyl substituted pseudo-isocyanines (PIC) dyes allow to form effectively the aggregates without stabilizing by polymers. These films have a high value of cubic optical nonlinearity but the nonlinear properties are decreasing during some months. It is important to have more stable films for application, for example, such as J-aggregates stabilizing by polymer. In this work thin solid films ( $\approx 100$  nm) of PIC J-aggregates were obtained by spin coating of the proper choice of organic-organic or water-organic mixture of the solvents and the optimal dye/polymer weight ratio. We have used three different types of polymers such as hydrophobic polymethylmethacrylate, amphiphilic polyvinylpyrrolidone and hydrophilic poly-(sodium-p-styrenesulfonate).

The dispersion of the nonlinear susceptibility  $Im\chi^{(3)}(\lambda)$  of obtained films was measured by pump - probe method. The optimum ratio dye/polymer at which the protective properties of a polymeric matrix are implemented and high optical and nonlinear-optical properties of J-aggregates are achieved is found. The maximal value of  $Im\chi^{(3)} \sim 10^5$  esu together with technological advantages of the polymer protected J-aggregated films makes the obtained films attractive for the application in optical devices.

It was found that the values of cubic optical susceptibility strongly depend on the line width of exciton absorption. Two kinds of methods to change the width of J-peak were used. The first one is founded on the addition of another organic cations to the initial organic solution of PIC dye. The second one is based on the decreasing the sample temperature from 300 K till 77 K. The nonlinear absorption coefficient of an ensemble of J-aggregates with different width of J-peak is measured by Z-scan and pump-probe technique. Experimental results show the power dependence of nonlinear optical susceptibility ( $\chi^{(3)}$ ) on the width of J-peak ( $W$ ) as  $\chi^{(3)} \sim W^{-1.53 \pm 0.23}$ . The exciton delocalization length  $N_{del}$  can be determined from the absorption line width  $W$  [3]. Using this approach we evaluate scaling dependence of nonlinear susceptibility on exciton delocalization length  $\chi^{(3)} \sim N_{del}^\gamma$  with  $\gamma \sim 2.3 \pm 0.2$ . Obtained results show an excellent agreement with theoretical prediction ( $\gamma = 2.36$ ) for the size-enhancement of nonlinear optical properties in one-dimensional molecular aggregates [4].

**Acknowledgments** : Financial support by the NWO 047.009.019 and RFBI 02-03-33336 grants is gratefully acknowledged.

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## Opto-Electronic Properties of Discotic Materials

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Discotic liquid crystals (DLC) are nanostructured materials with opto-electronic properties suitable for applications in light emitting diodes, photovoltaic devices or field effect transistors. In particular their unique tendency to self-assemble into columnar nanostructures, with charge carriers delocalized along the stacks, makes them attractive materials for photonics.

We have studied extensively several DLC: hexa(3,7-dimethyloctyl)hexa-*peri*-benzocoronene (HBC-C8,2), hexa(*n*-dodecyl)hexa-*peri*-benzocoronene (HBC-C12), hexa(4-*n*-dodecylphenyl)exa-*peri*-benzocoronene (HBC-PhC12) (described as *p*-type), and HATNA 4A, HATNA 4D, R-DISC and PEDI (assumed to be *n*-type, but the *n*-type conductivity in these materials was so far not verified experimentally).

Photoluminescence, thermoluminescence and photo-induced surface potential decay techniques were employed in investigations of thin DLC layers obtained by drop-casting. Analysis of the photo-induced discharge kinetics yields information on photogeneration yield and on photoconductivity. Comparison of the discharges for positive and negative polarisations gives the first experimental evidence, that R-DISC and PEDI are electron-transporting materials, in contrast to the HBC discotics showing *p*-type conductivity. These results show that it should be possible to construct photovoltaic devices made from these discotic materials.

In order to obtain aligned films of DLC we have used the so-called zone-casting technique. It was found that when the casting parameters are optimised, this technique yields in some cases anisotropic films with parallel orientation of nanocolumns and with "edge-on" orientation of discotic molecules, on glass as well as on SiO<sub>2</sub>/Si substrates, *i.e.* suitable for FET construction.

### Acknowledgements

This work was supported by the EC project *DISCEL*, Contract No. G-5RD-CT-2000-00321.

The authors are grateful to Dr. A. Tracz (CMMS PAS, Lodz, Poland) and Prof. T. Pakula (MPI-P, Mainz, Germany) for their help in preparation and characterisation of anisotropic films.

# Microcavity Polaritons in Disordered Organics

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We theoretically analyze the photoluminescence (PL) and the spectrum of the polaritons in a microcavity, which contains a disordered organics. We show that the resonance between the cavity photons and the molecular transition  $E_0$  in an organic dye results in the appearance of the two polariton branches analogous to the polaritons in well studied inorganic semiconductors.

However, in the case of disordered organics the lower polariton branch exists only for small wave vectors  $\mathbf{q}(\underline{R})$ , where  $\underline{R}$  is the mean distance between the molecules of the dye. For other excited states the exciton-photon coupling is not important and these excited molecular states are incoherent like molecular excited states in the bulk disordered organics. The number of low branch coherent states is small in comparison with the number of incoherent states and the same picture takes place also for the next excited molecular states with the energy equal  $E_0 + n E_0 + n \omega_0$ ,  $n = 1, 2, 3, \dots$ , where  $\omega_0$  is the frequency of intramolecular vibration.

Using this physical picture and taking into account that in organic microcavity the energy of the Rabi splitting the same as the energy of intramolecular phonons can be order of 100meV we examine the decay of the upper cavity polaritons accompanied by the emission of an intramolecular phonon having the energy approximately equal to the energy of the Rabi splitting. The main contribution to this nonradiative decay rate arises from the transition to lower energy incoherent states.

We find that for a microcavity with cyanine dyes investigated in the works by Lidzey et al. (Sheffield, UK), the obtained transition time  $\tau \sim 50$  fs is in good agreement with the rough estimations made previously in mentioned experimental paper. We argue that at nonresonant cavity excitation the photoluminescence from incoherent states pump the coherent states of lower and upper branches of polaritons.

However, the short nonradiative life time of upper branch polaritons decrease a population of these states and consequently decrease its contribution to the intensity of photoluminescence from the microcavity.

# Organic and Metallic Photonic Crystal Nanostructures for Tunable Photonic Devices

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Optical photonic crystals have periodicities in dielectric contrast on the scale of optical wavelengths. Novel features result from such periodicities, including photonic band gaps and intra-gap states that can be used for manipulating light in optical circuitry, just as analogous electronic features are used for semiconductor devices. Reflecting interest in both photonic crystal properties and applications, enormous effort has been devoted to fabricating photonic crystals, which we will describe in introduction to this talk. While most of this work has been on all-dielectric photonic crystals, equally interesting properties arise for metallo-dielectric photonic crystals, which can comprise periodic metal sphere arrays or metal meshes interpenetrated by a dielectric or vacuum. These properties include omni-directional reflectivities higher than for bulk metals, and metallic structures that are optically transparent even when the layer thickness is much greater than the skin depth, as we have demonstrated for 3D inverted opals.

One popular fabrication method for three-dimensional photonic crystals is by the self-assembly of colloidal spheres, which is the process that nature uses for forming structurally related natural opal. Depending upon the composition and structure of the targeted photonic crystal, subsequent infiltration and extraction steps are used to provide a photonic crystal that is either the direct or inverse lattice of the original close-packed array of colloidal spheres. While the direct and inverse photonic crystal can be viewed heuristically as resulting from the packing of chains (one-dimensional photonic crystals) or two-dimensional sheets (two dimensional photonic crystals), no methods have been described for decomposing three-dimensional photonic crystals into these lower dimensional components. The availability of lower dimension photonic crystals could enable investigation of the effects of one- and two-dimensional periodicities on electronic, phononic, and magnetic properties. Possible applications could eventually be enabled, from fibrous photonic crystal colorants for plastics to one-dimensional photonic crystal wires for optical sensors and probes, which can be a few hundred nanometers in diameter and indefinitely long.

We will report in detail on our newly developed methods to create 1-D, 2-D and 3-D photonic nano-structures by advanced self-assembly, using particles of any size and oriented crystallization on Si-surfaces, patterned by e-beam lithography. We then templated them with practically any materials, both electrically conductive and insulating, including conducting polymers, magnets, ferroelectrics and so on. Such superlattices are photonic band gap (PBG) structures, in which we have achieved tunability by various methods, and demonstrated interesting properties, such as tunable intra-gap lasing, new type of combinational elementary excitations, called “Braggaritons”, and other. We were able to create new types of metallic photonic crystals, which are 1-D wires and separate 2-D metallic meshes, and most recently have created hydrogel inverted opals, which are very soft and can significantly change the dimensions upon dehydration caused by temperature, pH, etc.). Various applications of tunable PBG systems will be described.

# Hyperpolar Multichromophoric Nanoassembly for Molecular Nonlinear Optics

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**Keywords:** push-pull chromophores, cyclodextrin, electronic interaction, excimers, excitonic coupling, dipole moment, hyperpolarisability, self-organization

A multichromophoric nanoassembly was designed by gathering seven push-pull chromophores on a  $\beta$ -cyclodextrin assembling unit via covalent flexible linkers. Such supermolecule provides a valuable model for the investigation of confinement effects on the linear and nonlinear optical properties of push-pull chromophores in the condensed phase. Push-pull chromophores display a significant ground-state dipole, thus promoting strong dipolar interactions that are expected to influence both the conformation and the optical properties of the multichromophoric assembly. In addition electronic interactions between the large transition moments of the closed-packed chromophores can promote Frenkel-exciton-type coupling within the supermolecule.

In this perspective, the photophysical and nonlinear optical properties of the multichromophoric bundle were investigated and compared to those of the monomeric chromophore. The absorption, circular dichroism and fluorescence investigations provide evidence that the push-pull chromophores do not behave as isolated independent chromophores within the multichromophoric assembly. The nanoscale supermolecule is hypsochromically and significantly hypochromically shifted with respect to its monomeric analogue. In addition, the close proximity promotes excitonic coupling, as well as excimer formation phenomena. The nanoscopic assembly also shows a very large dipolar moment ( $\mu = 38$  D), and a significant molecular first-order hyperpolarisability, which reveal a spontaneous sheaf-type self-arrangement of the dipolar chromophores within the supermolecule. Such chiral hyperpolar nanoassemblies are promising candidates as model systems for nanophotonics.

# Photoinduced spontaneous patterning of azopolymer films: towards a new process for nanostructuration

C. Hubert<sup>1</sup>, C. Fiorini-Debuisschert<sup>1</sup>, P. Raimond<sup>1</sup>, J. M. Nunzi<sup>2</sup>

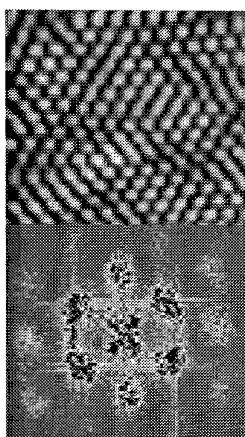
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During the last decade, large effort has been dedicated towards the miniaturization of devices for photonic applications mainly in the fields of information technology and telecommunications. Due to both their high molecular engineering potentialities and their relative ease of processing, organic materials appear as particularly promising for the design and implementation of new concepts for nanophotonics. One of the key point towards this objectif is structuration at the nanoscale level.

We provide in this work experimental evidence of spontaneous light-assisted submicrometer hexagonal patterning of the surface of azo-dye polymer films. This original and easy to set light-assisted patterning process should open new routes towards simple and fast realization of micro and nanometer structures.

Irradiation of an azopolymer film using a light interference pattern is now well known to lead to direct structuration of the film surface<sup>[1]</sup>. Substantial mass transport has been shown to occur from the irradiated to the non irradiated area, in conjunction with the light intensity gradient. More surprisingly, we show in the following that uniform irradiation of an azo-dye polymer by a single laser beam with normal incidence on the polymer film surface leads to a self structuration process resulting in the formation of a quasi hexagonal grating<sup>[2]</sup>.



As shown in the upper part of the figure, structures appear as peaks regularly spaced out. By considering six peaks, we can define hexagon which main axes are oriented along the light polarization direction. As can be shown on the Fourier transform of the structures (lower part of the figure), three principal axes are identified which confirm the hexagonal organization of the doms and the creation of a two dimensional grating. It has been observed that the orientation of these hexagons can be controlled by the polarization direction of the laser beam. The influence of parameters such as the laser intensity, the irradiation time, the thickness of the polymer film but also the irradiation wavelength has been studied and seems to indicate that one possible origin of this hexagonal self structuring could be spatio-temporal instabilities effects originating from interferences in a non-linear medium, following an optical feedback phenomenon. Other experiments are under way to confirm such origin but also to determine the relevant parameters governing such original light-induced structuring process. A total understanding of the process could permit to go further with this top down structuration approach considering more particularly the realization of more complex structures.

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# Sub-microscopic nonlinear optical probing of organized molecular assemblies

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Molecular photonics is currently emerging as an attractive field capable of fulfilling the requirements of a wide variety of applications such as ranging from information technologies to biotechnology, with specific assets pertaining to functional molecules and polymers.<sup>1</sup> In order to provide relevant organic materials based solutions to the demand for a broad variety of key photonic functions of interest for telecom as well as life sciences including luminescence, lasing, nonlinear optical phenomena, photo-induced transport, detection and others, the control and monitoring of molecular organization from the nanoscopic to the macroscopic scale appears as an all-pervading issue of central importance. Along these lines, molecular engineering for nonlinear optics has been enriched by the possibility to explore and design molecular materials at the nanometer scale, based on supra-molecular arrangements<sup>2</sup> or micro- and nano-patterning techniques.<sup>3</sup> Moreover, in order to enable developments in supra-molecular science, the need to down-scale observation techniques beyond the diffraction limit has triggered developments in near-field and nonlinear optical microscopy.

We present in this work high resolution two-photon excitation microscopy studies using both two-photon fluorescence and second harmonic generation (SHG) in order to probe molecular organization and nonlinear optical responses at sub-micron scales in different environments. This technique entails both spectral and polarization resolutions so as to provide local tensorial informations pertaining to complex molecular angular distribution and related symmetry features. In particular, SHG is an ultra-sensitive quasi background-free probe of local non-centrosymmetric components to any complex molecular angular distribution. Our current experiment consists of a 120 fs-pulsed source excitation at a fundamental wavelength of  $\sim$ 1020 nm, implemented in an inverted microscope set-up with a high numerical aperture objective, yielding a spatial resolution of 300 nm in the detected visible spectral range. SHG and fluorescence mapping of  $10 \times 10 \mu\text{m}$  areas provide evidence of oriented domains in molecular monolayers deposited by the Langmuir-Blodgett technique. The angular distribution features of local molecular assemblies can then be clearly inferred from the local multi-linear polarization response.

Such studies were also implemented in guest-host low- $T_g$  polymer films where we report the local dynamics of molecular orientation under electric field at room temperature. In this configuration, planar electrodes provide an in-plane field which couples to the molecular dipole and leads to a non-centrosymmetric molecular angular distribution. The polarization of the SHG response is then a quantitative and unambiguous signature of local environmental features accounting for the molecular distribution as well as a map of the poling potential with sub-microscopic resolution. Such studies open perspectives towards probing of electro-optic devices at corresponding sub-micron scales. This technique is being also currently applied to complex structures such as nano-structured metal thin films displaying a pseudo fractal morphology. Such structures concentrate very large electromagnetic waves in nanometer sized plasmon sustaining areas. We have thus evidenced local surface SHG enhancement on granular gold substrates<sup>4</sup> obtained from a high vacuum metal evaporation technique. The enhanced response and related localization and polarization features are shown to depend strongly on the granularity of the samples, thus demonstrating the relevance of sub-micron SHG to map-out the surface morphology.

These results open-up challenging perspectives towards electrical or optical monitoring of molecular assemblies at sub-microscopic size including nano-objects. The use of SHG microscopy as a sensitive probe for molecular molecular arrangements may be further extended to nano-structured materials with hybrid properties, reduced scale lasing cavities or complex media of biological interest, the latter of great current interest.

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# Investigation of anomalous light propagation in discrete optical media

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Discrete (as compared to homogeneous) optical media are characterized by spatially varying refractive index distributions leading to light propagating in optically coupled channels, like e.g. in an array of waveguides.

In the first part the fabrication of discrete optical media in uv-curable material is thoroughly

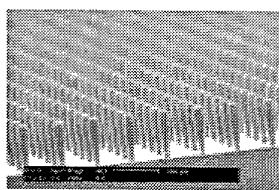


Figure 1: 3D Micro-optical structure

studied starting from conventional uv-polymerization up to 3D micro-optical structure formation in these materials due to controlled self-writing processes. A locally deposited amount of energy during the material exposure leads to a local non-linear change of the refractive index. This results in self-focusing and self-guiding effects which, e.g. can be used for the fabrication of high aspect ratio conic structures (cf. Fig. 1).

In the second part it is proved experimentally that light propagation in an array of coupled monomode waveguides (Fig.2) exhibits striking anomalies /1/: refraction is a periodic (instead of a linear one like in homogeneous media) function of the initial tilt of the beam (Fig. 3). Diffraction can be controlled in size and sign by the input conditions. Diffractive beam spreading can even be arrested and diverging light can be focused by the waveguide array. All these results are theoretically explained.

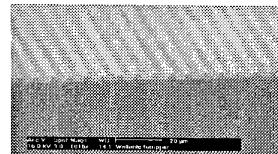


Figure 2: Measured refraction vs input tilt



Figure 3: Waveguide array

**3 2 1 0 1 2 3**

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# All optically induced frequency doubling process with periodic modulation of the nonlinear susceptibilities

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All optical poling technique allows purely optical orientation of dye molecules in a polymer matrix. The experiment consists of two steps: the writing (so called "seeding") period and the readout one. In seeding phase two beams, the strong fundamental one ( $\omega$ ) and weaker second harmonic (SH,  $2\omega$ , the  $2\omega$  frequency being located in the absorption band of the material) irradiate the sample and due to the coherent interference between them the second order  $\chi^{(2)}$ -susceptibility grating is encoded, with a period satisfying the phase matching condition for SH generation. During the readout step only the fundamental beam irradiates the sample and the second harmonic beam generated by the optically active medium is observed at the sample output. The coherent joint one- and two-photon absorption of two beams at  $\omega$  and  $2\omega$  frequencies results in a polar field  $E(t)$  ( $E(t) = E_\omega(t) + E_{2\omega}(t)$ ) inside the material, which is responsible for breaking the centrosymmetry of the medium. More precisely, the third-rank temporally averaged tensorial product of the field:

$$\langle E_{2\omega}^* \otimes E_\omega \otimes E_\omega \rangle$$

is non-zero, which can lead to an electronic orientation-selective excitation of the molecules. The physical origin of the effect lies in the orientational hole-burning in the initially isotropic distribution of dye molecules. Efficient all optical poling requires optimisation of the seeding beam intensities and the phase difference between them. We present an easy method of orienting molecules, leading to the presence of the quasi-phase matched second order nonlinear susceptibility  $\chi^{(2)}$  gratings with periodic spatial modulation of the second order nonlinear coefficient of the material. This new technique is applied to several dye-polymer systems.

# Characterization of nonlinear optical parameters of metal-doped polyvinylpyrrolidone nanostructures and organic dye molecules

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The results of third-order nonlinear susceptibilities studies of Fe- and Zn-doped polyvinylpyrrolidone (PVP) in processes of third harmonic generation of Nd:YAG laser radiation are presented. Nonlinear susceptibilities ( $\chi^{(3)}(-3\omega; \omega, \omega, \omega)$ ) of PVP:Fe and PVP:Zn were calculated to be  $5 \times 10^{-13}$  esu and  $3 \times 10^{-13}$  esu respectively. Third harmonic conversion efficiencies in these metallocomplexes were measured to be  $8 \times 10^{-7}$  and  $5 \times 10^{-7}$  respectively. We applied the Z-scan method to determine Kerr effect influence on frequency conversion process. The value of nonlinear refractive index of iron-doped PVP at the wavelength of  $\lambda = 1064$  nm was measured to be  $n_2 = -6.7 \times 10^{-13}$  esu. The influence of high-frequency Kerr nonlinearities in PVP:Fe was negligible on the  $I_{3\omega}(I_\omega)$  dependence.

We have studied the nonlinear optical properties of cobalt-doped PVP. The optical limiting studies have shown that this process was due to self-defocusing at the wavelength of 1064 nm and due to reverse saturable absorption and self-defocusing at the wavelength of 532 nm. Nonlinear absorption investigations have shown the absence of last process in infrared range, whereas in visible range the nonlinear absorption was considerable. It was shown that the main parameter influenced on the nonlinear process of picosecond radiation interaction with such media is the cobalt concentration in PVP. The results of nonlinear optical characteristics ( $n_2$ ,  $\chi^{(3)}(-\omega; \omega, \omega, -\omega)$ ,  $\beta$ ) measurements of investigated medium are discussed.

We also present the theoretical calculations of nonlinear susceptibilities, responsible for the frequency conversion and self-interaction effects, and of nonlinear refractive indices of organic dyes. The values of third- and fifth-order nonlinear susceptibilities responsible for the THG of Nd:YAG laser radiation ( $\lambda = 1064$  nm) are calculated on the basis of free electron model. In particular, the nonlinear susceptibilities  $\chi^{(3)}(-3\omega; \omega, \omega, \omega)$  of paraterphenyl and pentacene were calculated to be  $2.4 \times 10^{-30}$  esu and  $1.7 \times 10^{-30}$  esu respectively. The relation between the length of conjugated bonds of organic dyes and their third- and fifth-order nonlinear susceptibilities has been analyzed. Calculations of third-order Kerr-induced nonlinear susceptibilities and nonlinear refractive indices of organic dyes are presented. It was shown an importance of Kerr-induced nonlinearity influence on phase-matching conditions of the frequency conversion in tetracene and pentacene. The opportunity of some of organic dyes applying as the optical limiters was considered due to their high negative value of  $n_2$  ( $-1.5 \times 10^{-28}$  esu for pentacene).

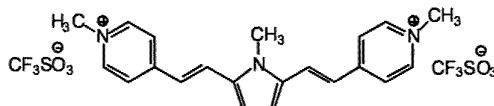
# Novel Heterocycle-Based Two-Photon Absorbing Dyes

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Organic molecules which can simultaneously absorb two or more photons (TPA) to be promoted to their excited states have recently been the subject of much research work in the scientific community due to the growing interest in advanced photonic applications such as two-photon laser scanning fluorescence microscopy, optical limiting, three-dimensional optical storage, microfabrication, and upconverted lasing.<sup>[1]</sup> In order to meet market criteria, molecules with large TPA cross-sections  $\sigma$  are required. It is now apparent that an appropriate design strategy involves symmetrically substituted systems having a general structure of the type D- $\pi$ -D or A- $\pi$ -A (A=acceptor, D=donor,  $\pi$ =conjugated moiety). Although a number of efficient TPA dyes are now available, the vast majority of these systems rely on benzenoid derivatives and simple primary organic functionalities. Indeed, it should be considered that electron-poor and electron-rich heterocycles may act as efficient acceptor and donor moieties. Furthermore, the intrinsic tailoring nature of the heteroaromatic rings makes these systems particularly appropriate to finely tune electronic and optical properties. We have recently reported the design of new heterocycle-based push-pull dyes<sup>[2]</sup> and prepared new NLO-phores with large second-order NLO<sup>[3]</sup> and frequency upconverted lasing activities.<sup>[1]</sup>



<sup>1</sup>

We herein report the synthesis, linear optical absorption and fluorescence, TPA properties, and TPA-based optical limiting activity of a novel series of heterocycle-based two-photon dyes, such as **1**.<sup>[4]</sup> These systems exhibit one of the largest TPA values so far known in the femtoseconds regime (TPA cross section as high as  $150 \times 10^{-50} \text{ cm}^4 \text{ s photon}^{-1} \text{ molecule}^{-1}$ , 150 fs laser pulses, 790 nm). Their TPA-based optical limiting activity is also shown. We present a combined UV-Vis, multinuclear NMR and Z-scan TPA spectroscopy study as a useful tool for the design of molecular systems with enhanced properties.

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## Related Photo, Thermal, and Charge Injection Driven Processes and Devices based on Single Walled Carbon Nanotubes

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Geoff Spinks<sup>3</sup>, Norm Barisci<sup>3</sup>, Gordon Wallace<sup>3</sup>

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The use of light for powering carbon nanotube-based thermoelectrochemical power generators and mechanical actuators is described, which builds upon our work on using carbon nanotubes for actuation, thermal energy harvesting, and energy storage. The work described will start from fundamental aspects related to nanotube properties in electrolyte and dielectric environments, move on to fabrication methods and measured properties, and end with performance analyses of device prototypes.

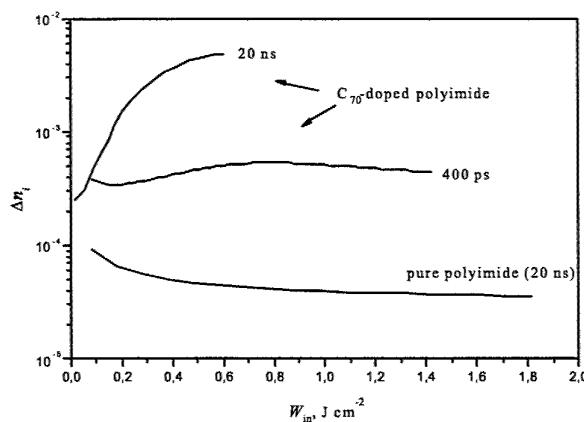
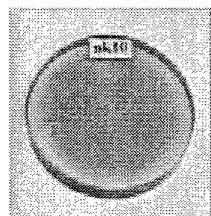
# Nonlinear optical study of fullerene-doped conjugated systems: a new materials for nanophotonics applications

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Organic nanophotonics problems have stimulated research in designing new materials for effective optical limiting and holographic recording systems, as well as good modulated media for information processing. Great interest has been expressed in nonlinear optical properties of organic conjugated systems doped with fullerenes [1-3]. The optical properties, which are conditioned by excitation of  $\pi$ -electrons, demonstrate that a new charge transfer complex is formed between fullerene and a donor fragment of an organic molecule. This complex is of a higher excited state absorption cross section than the ground state one. That is why, fullerene-doped systems are reverse saturable absorption materials and may be used for a sensor and eye protection as a nonlinear optical absorber. Moreover, a large value of the light-induced change in refractive index in these compounds contributes significantly to the optical limiting effect (due to energy losses by diffraction) and explains holographic recording in these media because of the photorefractive effect even without an electrical control. It also predicts large nonlinear refraction  $n_2$  and third order susceptibility  $\chi^{(3)}$ , which allow the materials to be used for conversion and modulation of a laser beam over broad spectral range.

In the present paper the nonlinear optical properties have been studied in the  $C_{60}$  and  $C_{70}$ -doped organic thin films (polyimide, 2-cyclooctylamino-5-nitropyridine, *N*-(4-nitrophenyl)-(L)-prolinol etc..) under a laser irradiation at wavelengths of 532, 805, 1315 nm. Photograph of the sample and laser-induced changes in refractive index of the fullerene-doped polyimide structure (at  $\lambda=532$  nm) are shown below.



For these materials the nonlinear refraction  $n_2$  and the third order susceptibility  $\chi^{(3)}$  were determined. They were  $n_2 \sim 10^{-10} \text{ cm}^2 \text{W}^{-1}$  and  $\chi^{(3)} \sim 10^{-9} \text{ esu}$  for thin films of the fullerene-doped organic structures,  $n_2 \sim 10^{-9} \text{ cm}^2 \text{W}^{-1}$  and  $\chi^{(3)} \sim 10^{-8} \text{ esu}$  for thin films of the polymer-dispersed liquid crystal compounds. Moreover, it has been found that the system can be applied as the laser power attenuator at the laser energy density of more than  $1.5-2 \text{ J cm}^{-2}$  and at the laser energy density up to  $0.8-1 \text{ J cm}^{-2}$  over the visible and near infrared spectral range, respectively. These materials can be used for a laser frequency conversion.

**Acknowledgments:** This work was supported by the ISTC Project # 1454 "Optical Barrier" and the Russian Foundation for Basic Research Grant # 00-15-99067.

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## Conduction and Optical Properties of DNA

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Because of the  $\pi$ -electron overlap on adjacent bases in a DNA molecule an electron or hole on the base stack is expected to move in response to a concentration gradient or an electric field. The resulting conduction has been measured by many groups, with widely different results. Their results range from DNA being a good conductor, even a superconductor, to its being an insulator. With a large gap, according to optical absorption measurements, DNA should have no carriers unless they are introduced at the contacts by an electric field, by light or by doping. Unintentional doping may account for the very large conductivities that have been seen.

Currently there is not agreement on whether the wavefunction of a carrier is limited to one base (or base-pair, more accurately), or whether it is spread out over a number of bases as a polaron to minimize its energy. Experiments in which a single carrier is introduced to a DNA molecule (in a solution of water and ions similar to that with which it is surrounded *in vivo*) have been interpreted as showing that conduction takes place by tunneling, incoherent hopping or polaron hopping or drift, the local base sequence determining which of these mechanisms predominates. The polaron mechanism has been shown to account well for shallow traps in DNA.

Attempts are being made to dope DNA controllably to increase its conductivity. That would enable making use of its self-recognition properties for self-assembly of nanocircuits in which it also provided the wires.

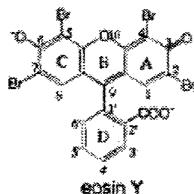
Optical properties of DNA, such as fluorescence and dichroism, will be discussed.

## Dynamics of Eosin Y encapsulated in a fourth generation functionalised POPAM dendrimer

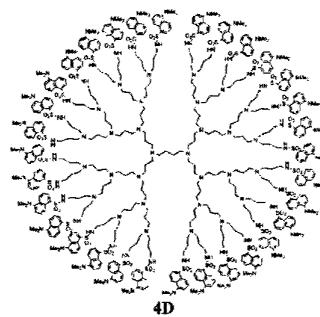
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We use molecular dynamics (MD) techniques to investigate the encapsulation of eosyn Y



in a fourth generation of poly-propylene amine, POPAM, dendrimer functionalized in the periphery with fluorescent dansyl units, which consists of 1542 atoms.



Using a large periodic box including up to 7 Eosin Y's and 3060  $\text{CH}_2\text{Cl}_2$  solvent molecules we examine the MD of these systems for 0.32 ns.

We find that a single guest molecule can be located in 4 different sites which are responsible for the two fluorescence lifetimes of the dye observed experimentally. Dynamics with an excess of guest molecules results in their expulsion and reduction to the experimental limit of 6 guests, with several of them located on the surface of the functionalised dendrimer. The close correspondence of the theory with experiment suggests that these methods can be used to design such systems in advance of experiment.

# Protein nanostructures light control for data storage

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Biophotonics can be considered as the crossing of photonics physics, and biotechnology. A few years ago by a collaboration between our laboratory and the laboratory of the Strasbourg School of Biotechnology, we have identified a method and process for producing specific proteins molecules adapted to some expected photonic uses by local light speed modulation by changing the genetic code of bacterias producing these molecules. This approach was patented. Later, we have found that natural source of protein can be considered by selecting protein for photonics use in the animal and vegetal world and some processing. We introduce the way to dope these extracted proteins for being light sensitive at the quasi molecular level.

Through light molecular protein interaction, we show that for a selected wavelength it is possible to structure in a volume a protein layer with a modulated wavefront.

Once we have light modulated a protein layer, we show how this layer can behave like a perturbated photonic crystal. We have attempted to introduce a signal in these perturbations. We describe how we code it for data loading and how we retrieve it for realizing terabit ROM data storage.

We conclude by perspective of the work in progress for developing protein RW memory and biophotonics component.

## Acknowledgments

The authors thank PIONEER Company for its assistance to this project that lead to 10 ULP-PIONEER international patents filed.

The authors thanks also the French German Rhenaphotonics organization for the contribution.

## Localizing single molecules and watching them interact

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A special feature of a single molecule is that it is a model system for a point dipole with a well-defined location, orientation and emission characteristics. We report on our recent experiments where we have combined single molecule spectroscopy and scanning probe microscopy to locate molecules embedded in a matrix with unprecedented three-dimensional accuracy. We apply strong electric field gradients at the end of a scanning probe electrode and induce Stark shifts in the absorption spectrum of the sample molecules. As the sample is scanned, a spatial map of the electric field distribution is obtained, allowing us to locate single molecules with nanometer accuracy.

In this context we will address the outlook for achieving "molecular resolution" in fluorescence microscopy and present some ideas for the use of cryogenic single molecule spectroscopy to structure biology.

In the second part of the talk I will discuss how we have used our single molecule localization techniques to identify two individual molecules placed very close to each other, undergoing a dipole-dipole coupling. We will give a detailed account of the comparison between the experimental results and the theoretical predictions regarding the modification of the spontaneous emission rate as well as the emission photon statistics from this system.

In closing, we will elaborate on ways to realize on-command manipulation of the dipole-dipole interaction between several molecules.

# Photon Statistics of a Triggered Single Photon Source

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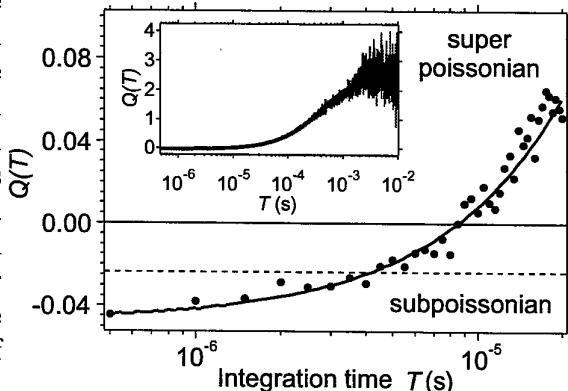
During the past few years, the realization of a triggered single photon source (SPS) has attracted much attention, mainly motivated by application in quantum cryptography [1]. We realized such a SPS relying on the pulse saturated emission of a single cyanine dye molecule embedded into a polymer thin film (PMMA). The emitted photons are efficiently detected by optical confocal microscopy.

We studied the fluctuations of the number  $N$  of detected photons, coming from our SPS, during a period of observation  $T$  [2]. By recording every photocount, we directly measured over 4 orders of magnitude of observation timescale  $T$ , the Mandel parameter [3] of the detected photons  $Q(T) \equiv \langle (\Delta N)^2 \rangle_T / \langle N \rangle_T - 1$ , where  $\langle \rangle_T$  has to be understood as a mean value over a set of measurements lasting  $T$ .

The opposite figure shows that, on timescale of a few excitation periods, subpoissonian statistics ( $Q(T) < 0$ ) is clearly observed. The measured value is consistent with an overall quantum efficiency  $\eta = 4.5\%$ . We also showed that the probability of two-photons events is 10 times smaller than what is observed with poissonian photocount statistics obtained with strongly attenuated laser pulses. On longer times, blinking in the fluorescence, due to the molecular triplet state, produces an excess of noise corresponding to  $Q(T) > 0$ .

We developed a simple model to account for this global behaviour. In this model, the molecule is either available for fluorescence and is said to be in a ON state, or it is in its triplet OFF state and does not fluoresce. The solid line on the above figure is a fit to the data according to this model.

Such an exploitation of the set of photocount records can be straightforwardly applied to study intensity fluctuations of other single photon sources, realized with semiconductor nanostructures or single quantum emitters. This technique is also suited to investigate time-resolved photochemical properties at the single molecule level (intersystem crossing dynamics, excitation transfer in molecular assembly).




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## Single molecule current switch – state of art

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A scheme of optically controlled current switch is put forward based on electrical properties of a molecular wire containing chemically attached photochromic side groups [1,2]. Upon changing the dipole moment of the photochromic units by light of a suitable wavelength, energies of electrostatic interactions of charge carriers on the conjugated polymer chain ('molecular wire') and the dipoles are locally modified. These changes result in the formation of a potential wall structure, creation of local states for charge carriers on the molecular wire, and hence in a decrease of the on-chain carrier mobility. Alternatively, a similar effect may arise due to a suitable change of either the ionization energy or the electron affinity of the polymer segment containing the chemically attached photochromically active side group.

The idea is based on results of electrostatic calculations of local states for charge carriers formed in the vicinity of dipolar species (presented in the accompanying contribution [3]) and has been supported by *ab initio* quantum chemical calculations of molecular potentials. Results of model macroscopic measurements of drift charge carrier mobilities in thin films of unsubstituted poly[methyl-(phenyl)silylene] (PMPSi), and copolymer containing polar benzaldehyde 2,4-dinitrophenyl-hydrazone groups (PMPSi-DNPH) [4] are also presented.

### Acknowledgments

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# Electroactive molecular devices with carrier mobilities modulated by light: an electrostatic approach

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Transport of charge carriers in molecular materials is often controlled by local states (traps) formed by chemical and/or structural defects. The mechanism of formation of the traps can be explained within a model [1,2] based on the electrostatic approach developed by Lyons [3,4]. According to the model, the energy of a state allowed for a carrier localized on a molecule is a superposition of a molecular parameter (ionization energy or electron affinity) and a contribution from electrostatic interactions between the localized carrier and surrounding polarizable molecules (polarization energy). A suitable local modification of any of these parameters results in a formation of traps for electrons and/or holes.

The electrostatic model can also be employed to simulate the situation often encountered in low-molecular weight materials and polymers, where polar species are dispersed in non-polar matrices. Suitable calculations [5,6] have demonstrated that traps as deep as ca. 0.4-0.5 eV can appear on sites adjacent to a polar molecule though the molecule itself does not necessarily form the trap. Both the depths and the cross sections of the traps formed in such a way were found dependent on the dipole moment. The latter feature offers a possibility of controlling the trap depths (and hence the carrier mobilities) by a modulation of the dipole moments of the dopants (e.g., by light). One may speculate that such materials can act as molecular switches performing their action on both microscopic and macroscopic level [7].

The contribution will present results of model calculations of molecular systems containing isolated and interacting polar dopants. Requirements for the molecular architecture of the switch resulting from the electrostatic model, results of quantum-chemical calculations and relevant experimental results will be discussed in the accompanying contribution [8].

## Acknowledgments

The financial support from the Polish State Committee for Scientific Research (grant No 4T09A 132 22) and the Grant Agency of the Academy of Sciences of the Czech Republic (grant A1050901) is gratefully appreciated.

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# Fluorescent Photochromic Diarylethene Oligomers

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Fluorescent photochromic materials collect strong interest for their possible application in optical memory and fluorescent probe.. In particular diarylethene having fluorescent chromophores have been reported to show interesting fluorescent photochromic properties and demonstrated as materials for non-destructive optical readout system. In this presentation we report synthesis and novel properties of diarylethene containing oligomers. Diarylethene containing oligomers were synthesized starting from 1,2-bis(2-methylbenzo[b]thiophene-3-yl)hexafluorocyclopentene (BTF6) with fluorescent builder. The resulting oligomers showed photochromic properties as shown in Figure 1. Interestingly strong emission at ~460 nm was observed from the oligomer dissolved  $\text{CHCl}_3$  solution, when excited with a 325 nm light. The fluorescence quantum yield of the oligomer was much higher than the starting diarylethene (BTF6) as shown in Figure 2. Both photochromic response and fluorescence quantum yields of the oligomer were increased as compared to those of BTF6. Such a result could be explained by anti parallel type diarylethene structure in oligomers, in which the population of photo active conformers are much higher as compared to BTF6. Further characterization and fluorescent properties of diaryethene oligomers will be presented.

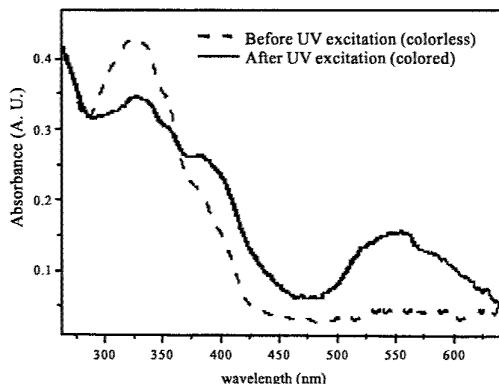


Fig 1. Photochromic spectral change of diarylethene oligomer in  $\text{CHCl}_3$  solution ( $1 \times 10^{-5}$  M)

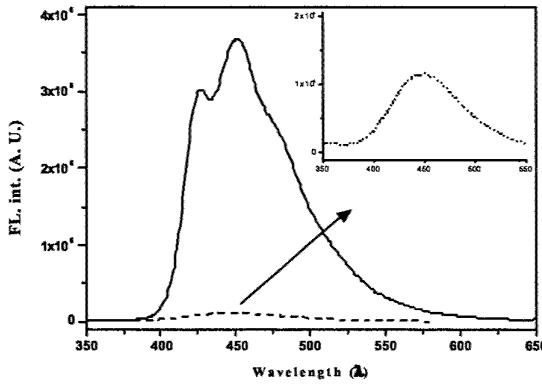


Fig 2. Fluorescence spectra of diarylethene oligomer (solid line) and BTF6 (dashed line) in  $\text{CHCl}_3$  solution.

# Photoreactive calixarene polymers for photonics applications

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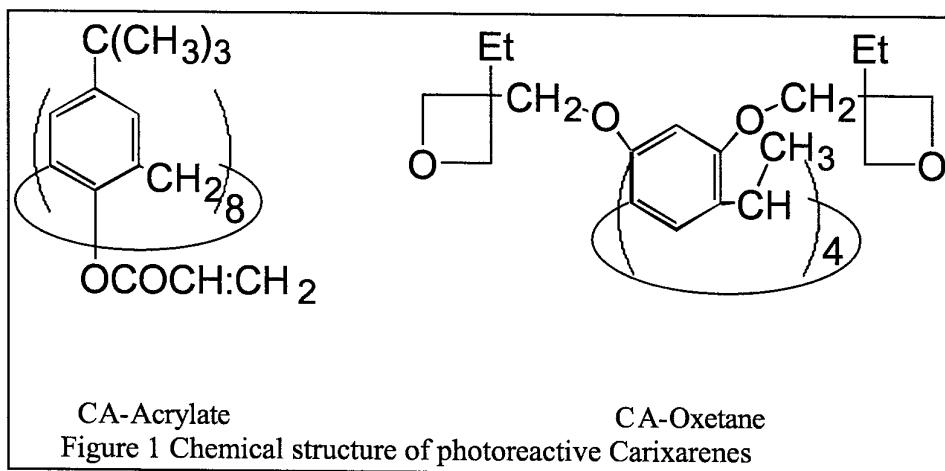
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Photoreactive calixarene derivatives are attractive material for photonic applications because they are very stable in high temperature conditions and have a potential to act as baskets for specific molecules. Such calixarene derivatives are recently synthesized from p-tert-butylcalixarene or methylcalix resorcinarene in good yields<sup>(1)</sup>. Among them we have selected p-tertbutyl calix[8]arene acrylate (CA-acrylate) and tetramethyl-octakis(3'-ethyl-3'-oxetanyl-methoxy) calix[4]resorcinarene (CA-oxetane) and checked the conversion of the these photoreactive carixarenes,

Figure 1 shows the chemical structure of the novel photoreactive calixarenes. They are polymerized by adding photopolymerization initiator under the irradiation of high-pressure mercury lamp. These photoreactive calixarene derivatives containing acryloyl or oxetane groups with varied monomers were photopolymerized successfully. Their thermal and optical properties such as glass transition temperatures, refractive index, and propagation loss of their films are investigated. They have excellent thermal stability at 250° or more. When CA acrylate derivatives were polymerized with trifunctional methacryloyl group containing monomer, the refractive index and the thickness of the polymer film are not influenced by the conversion and showed a constant value. The propagation loss is 1.5 dB/cm at 1,300nm and is almost equal to that of PMMA (~1dB/cm). Hence, all these properties satisfy this polymer to be a good candidate for optical application. We have also investigated the possibility of the calixarene polymers that contain nonlinear optical chromophores.



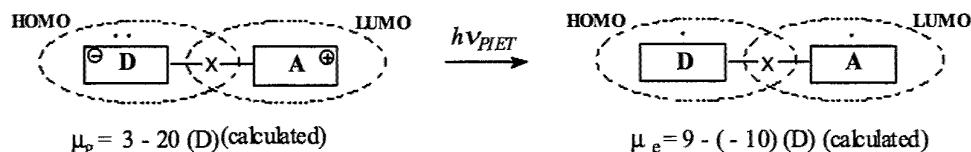
# The search for highly polar betainic type molecules for electro-optical applications

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The search for non-linear optical materials commonly is limited by synthesis of new push-pull molecules with diverse electron donor and electron acceptor substituents connected by conjugated linkers. Our approach is different of commonly used. We aimed to synthesize bipolar intramolecular salts—betaines, comprising in molecule electron donor anion part and electron acceptor onium cation part, connected directly or by conjugated linkers. Such betaines possess large electric dipole moment, are subject to photoinduced intramolecular electron transfer (PIET), giant change in electric dipole moment in the excited state and considerably hyperpolarizability, which causes large non-linear optical effects in solution, LB-films and in polymer matrix.



Quantum chemical calculations of mentioned betaines showed, that the HOMO and LUMO are strongly localized but in the same time overlap a little, and an effective PIET can take place [1, 2]. The **A** moiety is an unsubstituted or substituted N-connected pyridinium ring, but **D** – C-connected anion of strongly CH-acidic 5-membered cyclic  $\beta$ -dicarbonyl compound. The linker **X** could be p-phenylene, or the **A** and **D** moieties could be connected directly. These betaines should form a molecule in plane.

Both calculation and experimental data show highly dipolar PIET in mentioned type of molecules, accompanied by the change of sign value of the dipole moment. This switching phenomenon is important for the optoelectronic effects including second harmonic generation. The macroscopic effect is determined by the number density of the embedded chromophores, their hyperpolarizability and their degree of noncentrosymmetrical orientational order. This net polarization is usually achieved by aligning the chromophore dipoles. From this point of view the preparation of highly ordered films are very important. The most popular are LB-multilayers, self-assembled monolayers and polymer films of these compounds. The betaines were oriented by corona poling in doped poly(methylmethacrylate) films. Some of the results will be presented in our report. The structure of the films are clarified through the AFM measurements.

The arrangement of the polar molecules in the film are expected to be clarified through the surface potential measurements. The surface potentials are governed by dipole moment of the ordered polar molecules in the film and are related to chemical structure, packing densities, molecular orientations of the molecules. The reversible surface potential changes under optical irradiation in the PIET band was observed.

Nearly all betaines are unstable on irradiation in the PIET band in solutions and host-guest polymer film due to possible photochemical oxidation by air oxygen. The rate of oxidation is dependent on structure of betaines. The main efforts in synthesis of novel betainic type compounds are targeted to prepare: a) good soluble compounds, b) photochemically more stable in solutions compounds, c) compounds having two hydroxyl or two carboxyl groups, or one hydroxyl and one carboxyl group – starting materials for soluble NLO polymers.

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# Intermolecular Charge Transfer Multilayers for Nonlinear Optical Applications

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Multilayers made from alternate very thin layers (typically 2 nm), of electron donating and electron accepting molecules were prepared by the OMBD technique. The studied structures were of ABABAB... and ABCABC... types, where layer A is made from electron accepting molecules ( $C_{60}$ ), layer B from electron donating (TPN, TPD or TPP) and layer C from neutral molecules ( $MgF_2$ ).

The second-order NLO properties of these multilayers were studied by the transverse optical second harmonic generation measurements. A significant increase of SHG intensity was observed in ABCABC... type structures, where an effective intermolecular charge transfer is expected with creation of a noncentrosymmetry in the perpendicular direction to the layers. The largest  $\chi^{(2)}(-2\omega; \omega, \omega)$  susceptibility was measured with multilayers containing rubrene (TPN). The SHG experiments performed on thin films with different thicknesses show that the nonlinear optical response comes from the bulk material and not from the interfaces. The observed quadratic dependence of SHG intensity on the input power shows that the charge transfer takes place at the ground state.

The third order NLO properties of these multilayers were also studied by the transverse optical third harmonic generation technique. No increase in  $\chi^{(3)}(-3\omega; \omega, \omega, \omega)$  was observed in comparison to the net materials.

## Two-photon isomerization of diaryethenes in films of poly-methyl-methacrylate

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We present experimental evidence of real-time two-photon isomerization (TPI) of 1,2-dicyano-1,2-bis-(2,4,5-trimethyl-3-thienyl)ethane, a diarylethene (DE) derivative that has two photoisomers (A and B) which are thermally stable at room temperature, in films of poly-methyl-methacrylate (PMMA).

The DE chromophores were introduced as guests into PMMA with 10 % weight concentration, and 7  $\mu$ m thick films were spin-coated on cleaned glass substrates, and TPI dynamics were performed in a pump-probe experimental arrangement. The pump beam was a regeneratively amplified Ti:Sapphire laser (wavelength: 775 nm, pulse duration : 2 ps, repetition rate : 1 kHz), and the probe beam was the 532 nm green light of frequency-doubled Nd:YVO<sub>4</sub> laser.

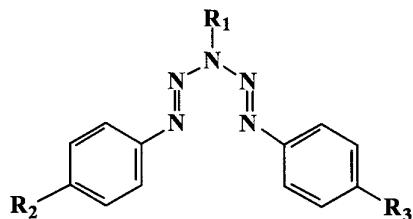
The DE/PMMA sample is totally transparent at the pump wavelength, and the probe light is absorbed only by the B isomer, and any increase in the sample's absorption at the probe wavelength upon pump excitation proves the creation of B isomer by a TPI process. The changes of the absorption spectra of the samples before and after pump excitation are consistent with chromophores isomerization induced by two-photon absorption. The slopes of the real-time dynamics of two-photon isomerization showed the square law dependence on the pump light intensity, and analytical expressions based on rate equations for two-photon photochromism have been developed to help interpret the experimental observations. TPI is a nanophotonic process that has potential for application in nanoscale optical data storage.

## Photosensitivity of some pentazadiene-1,4

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Photochemical investigations of some synthesised 1,5-diarylsubstituted pentazadiene-1,4 were carried out.



I. R<sub>1</sub> = -CH<sub>3</sub>, R<sub>2</sub> = R<sub>3</sub> = -H; II. R<sub>1</sub> = -CH<sub>3</sub>, R<sub>2</sub> = R<sub>3</sub> = -OCH<sub>3</sub>; III. R<sub>1</sub> = -CH<sub>3</sub>, R<sub>2</sub> = R<sub>3</sub> = -NO<sub>2</sub>; IV. R<sub>1</sub> = -CH<sub>3</sub>, R<sub>2</sub> = R<sub>3</sub> = -COOBu; V. R<sub>1</sub> = -CH<sub>2</sub>-CH<sub>2</sub>-OH, R<sub>2</sub> = R<sub>3</sub> = -H

Ethanol solutions of studied compounds were undergone an exposure by high pressure Hg lamp monochromatic light ( $\lambda=365$  nm) irradiation. Kinetics of pentazene photo dissociation were established and quantum yield values of photolysis were determined according potassium ferrioxalate actinometer method. Radical mechanism of photo dissociation was proposed based on analysis of photolysis products and quantum chemical calculations (semi empirical method CNDO/2 was applied). Photo dissociation of pentazene molecules is shown to proceed only with decreasing of molecular symmetry in dissociative state; after electron transfer into the lowest triplet state the final decomposition of molecule into N<sub>2</sub> and two radical products occurs. Dependence of quantum yield values upon the nature of substituents in phenyl ring correlates with the results of quantum chemical calculations.

Geometry of pentazene molecules was optimized and contributions of EE, EZ, ZZ isomers were estimated. EE-isomer was postulated to be predominant and under UV-irradiation partial isomerization available. This process to some extent is competitive with photo dissociation.



# POSTERS



# Real-time control of the all-optical poling process in polymer thin films

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The all-optical poling technique, a purely optical orientation method proposed by Charra et al. [1], enables the encoding of the light induced noncentrosymmetric second-order polarization in originally centrosymmetric materials, for which second order optical activity is normally forbidden due to symmetry reasons. This method is based on the interaction of the optical medium (polymer film containing chromophore molecules) with a strong fundamental electromagnetic field  $E_\omega$  and weaker second harmonic (SH)  $E_{2\omega}$  field, with the wavelength of the SH field being within the material absorption band. The physical mechanism is attributed to an efficient quasi-permanent photoinduced orientation of dye molecules following the orientational hole burning process induced by selective polar excitation through coherent one- and two- photon absorption mechanism. The centrosymmetry of the material is broken as the resulting optical field  $E(t) = E_\omega + E_{2\omega}$  has a nonzero third-rank time averaged tensorial product which leads to the orientation selective excitation of molecules undergoing subsequent repetitive photoisomerization cycles [2]. The whole phenomenon gives in consequence a noncentrosymmetric alignment of dye molecules, oriented in a given direction and sense. The experiment consists of two phases: the writing ("seeding") period and the readout one. During seeding two beams, the fundamental one ( $\omega$ ) and its second harmonic ( $2\omega$ ) are incident onto the sample and encode in the medium the second order  $\chi^{(2)}$  susceptibility grating with a periodicity satisfying the condition of phase matching for SH generation. In the readout period only the fundamental beam illuminates the sample and the second harmonic generation is observed at the sample output. The key parameters needed to obtain the highest efficiency of the all-optical poling process are the relative phase difference and the relative intensity ratio between the beams at fundamental and second harmonic frequency. If both these parameters are optimised, the maximal photoinduced susceptibility  $\chi^{(2)}$  is achieved at saturation [3]. We present a novel technique of non-perturbative monitoring of the all-optical poling orientation, an original stable one-arm interferometer which relies on the index dispersion of the optical glass. The new configuration of the experimental set-up permits all-optical poling of thin film materials without any necessity of taking into account the phase difference between seeding beams. This new technique is applied to several dye-polymer systems. We look for original mechanisms of SHG, which would not be based on the "common" photoisomerization *trans-cis*. Doping the neutral polymer matrix with electron-acceptor dye molecule gives no SHG, while in case of the electron-donating matrix (like polivinylocarbazole, PVK) SHG may result due to the transfer of electrons between the chromophore molecule and the polymer matrix. Our research is also devoted to the study of new polymer materials which may reveal better stability of the induced polar order than this of the Disperse Red 1, where 80 % losses are observed under the irradiation with the fundamental beam (photorelaxation) within the first hour after the seeding phase is stopped. We present a polymer system of excellent stability of the second order susceptibility  $\chi^{(2)}$  under strong irradiation at fundamental frequency, presumably due to the photoinduced crosslinking.

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# Molecular probes for nonlinear optical imaging of biological membranes

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Second-harmonic generation (SHG) and two-photon excited fluorescence (TPEF) are nonlinear optical (NLO) phenomena which scale with excitation intensity squared, and hence give rise to an intrinsic 3-dimensional resolution when used in microscopic imaging. Whereas TPEF microscopy has gained widespread popularity in the biology community for imaging at an increased penetration depth in tissue with reduced photodamage, SHG microscopy has only recently been demonstrated as a tool for high resolution biological imaging. Because SHG is a coherent phenomenon while TPEF is an incoherent phenomenon, the two provide intrinsically different contrasts. In particular, because of its sensitivity to local asymmetry, SHG microscopy promises to be a powerful tool for the study of membrane dynamics. Within this framework, we have implemented a molecular engineering approach towards NLO-probes specifically designed for SHG and/or TPEF nonlinear imaging of cellular membranes.

We have designed nanoscale rod-like or dumbbell fluorophores showing very large TPEF cross-sections in the visible red region, outperforming standard fluorophores such as fluorescein by up to two orders of magnitude. By grafting hydrophilic end-groups, *bolaamphiphilic fluorophores* combining high TPEF cross-sections and affinity for cellular membranes were obtained. Their incorporation and orientation in model or cell membranes can be monitored by TPEF microscopy.

Furthermore, amphiphilic push-pull chromophores combining both high TPA cross-sections in the near-IR region and large first hyperpolarizabilities were designed as NLO-probes for imaging of biological membranes by simultaneous SHG and TPEF microscopy. These NLO-phores offer intriguing potentialities for imaging of fundamental biological processes such as adhesion, fusion or for reporting of membrane electrical potentials.

**Keywords:** Two-photon absorption, TPEF microscopy, SHG microscopy, NLO-phores, molecular probes, cell membrane imaging, membrane potential.

# Mapping the dipolar radiation of copper nanoparticles using a photosensitive film

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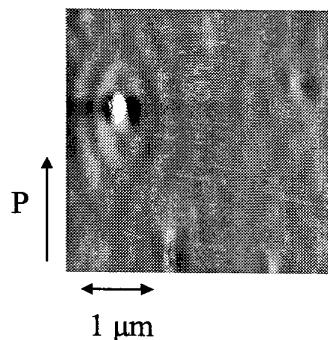
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Some years ago, it was discovered that polymer films containing azo-dye molecules (dissolved in a polymer host matrix, or grafted to it) undergo a permanent structuration under non-uniform laser illumination.<sup>1,2</sup> The polymer is expelled from high intensity areas and the film thickness modulation gives a negative image of the intensity map. It was interesting to utilize this property in order to evaluate the electromagnetic field intensity radiated by metallic nanoparticles submitted to a laser beam.

A film containing disperse-red molecules grafted on a PMMA matrix was spin-coated on a cleaved mica substrate (film thickness 870 nm) ; its roughness measured by AFM was found negligible. Then copper particles of ten nanometer diameter in suspension in toluene were deposited on the film (no modification of the film surface was induced by pure toluene). The film was submitted to laser irradiation ( $\lambda = 442$  nm,  $I = 0.2$  W/cm<sup>2</sup> for 20 mn). AFM scanning reveals a structuration of the film surface induced by the interferences between the incident laser beam and the dipolar radiation of the metal particles.



In fact copper particles aggregate to form islands containing about ten particles. In the figure is shown the AFM picture: areas of lower thickness appear darker and raised areas brighter. The laser polarization directions is indicated by the **P** arrow. The brightest spot on the left side is where the particles are located. Polymer is pilled under the metallic island.

The observed periodicity between deeps lies around 345 nm, which is smaller than the wavelength (442 nm). This reduction is likely to be due to the film refractive index ( $\sim 1.7$ ).

We could simulate the damped periodic structure by assigning  $\pi$  for the value of the phase of the metal island polarizability. According to the complex refractive index of copper at 442 nm, the correct value of a 10-nm particle should be  $\pi/5$ . This disagreement may arise from the interactions inside the island and its discotic shape.

Recently, H'dhili *et al.*<sup>3</sup> have studied the structuration of the surface of the same kind of film, induced by the interference pattern of a laser beam and the AFM tip itself, was surprisingly interpreted as a positive image of the intensity map (decrease of thickness on darker areas, and increase on brighter ones).

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# Magnetic and morphologic characterisation of some substituted ferrites synthesised by a non-conventional method

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The interest for preparation of substituted ferrites is generated by the fact that such materials have very interesting physical properties that lead to their applications as magnetic and electronic devices<sup>1-3</sup> as well as catalysts in processes like dehydrogenation<sup>4</sup>, oxidation<sup>5-8</sup> and methylation.<sup>9</sup>

It was observed that, small variation in the substitution degree of Fe(II) or Fe(III) ions leads to major changes of the magnetic and electric properties and also of the samples morphology.

This paper reports the syntheses of manganese, nickel and zinc ferrite  $M_xFe_{3-x}O_4 \cdot nH_2O$  (M: Mn(II), x:0.35, n: 0.4; M: Ni(II), x:0.38, n: 1; M: Zn(II), x:0.45, n: 0.35) by a soft chemical method using as starting materials magnetite and suitable acetates in aqueous medium.

These compounds have been characterised by elemental chemical analysis, thermal analysis, IR spectroscopy, X-ray diffraction on powder as well as Mössbauer spectroscopy and magnetic measurements at room temperature.

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# The investigation of the surface potential of betaine type dipolar doped polymeric films

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Organic dye-doped materials have received considerable attention because of their large dipole moments and optical nonlinearities. Amorphous dipole electrets for photonic applications contain chromophore dipoles (A- $\pi$ -D), which consist of acceptor (A) and donor (D) groups linked by a bridge of delocalized  $\pi$ -electron system. Non-linear optical and electrical properties are obtained by dipole orientation of active units.

In this work betaine-type (IPB) molecule was investigated. As a result of the asymmetry of charge distribution, molecules posses in the ground state a considerable permanent dipole moment [1,2].

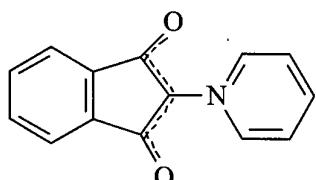


Fig.1 Structure of IPB molecule

dipole orientation of dye molecules in polymer matrices.

In our experiments, host-guest systems that have obvious advantages of synthetic simplicity were chosen. Optically transparent polymer poly(methylmethacrylate) (PMMA) was used as host. The different solvents (chloroform, acetone and DMFA) were used to deposit casted host-guest films onto gold, silver and ITO electrodes. The high-electric field corona poling was used to generate

Atom force microscopy and surface potential studies yield useful information regarding both structural and electronic properties of the films. The time constants of relaxation process of the surface potential of the corona poled films were of the order of several hours.

In this work we present results obtained from studies of poled films on the effect of heating. The thermally stimulated surface potential dependences on poling temperature were investigated. The  $\alpha$ - and  $\beta$ -relaxation processes of PMMA polymer influenced the value of the surface potential of the film. The effect of the different solvents on the thermal dependence of the surface potential are discussed.

The transition temperature, where no changes of the surface potential appeared, was related to glass transition temperature of the host-guest system.

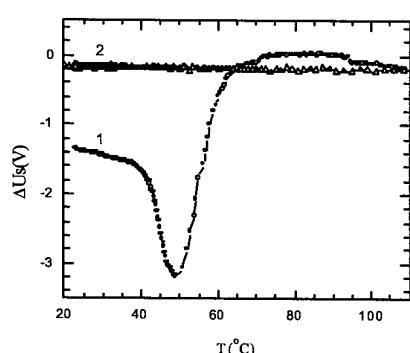


Fig.2 Thermal dependence of the surface potential on heating (1) and cooling (2) of the casted IPB-PMMA film on Au electrode.

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## 3D Characterization of Molecular Photo-Orientation: Application to All-Optical Poling and Liquid Crystal Polymers.

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Light is the best tool for the micro structuration of initially isotropic and homogeneous materials, such as functionalized polymers. Focussing or interference-patterning permit a spatial organization of optical properties, while the polarization of pumping beams allows an orientational order of actives molecules and produces unusual symmetries of the susceptibility tensor. A single polarized light beam induces anisotropy (birefringence and dichroism), i.e. a quadrupolar order. All-Optical Poling (AOP), produced by a simultaneous optical pumping with a strong pulsed laser ( $\omega$ ) and its harmonic ( $2\omega$ ), induces non-centrosymmetry. According to the polarization of both beams and the symmetry of molecules, the  $\chi^{(2)}$  nonlinearities are dipolar and octupolar, or purely octupolar. In addition to the non-centrosymmetric pumping ( $\omega/2\omega$  interference term), the one-photon excitation at  $2\omega$  and the two-photon excitation at  $\omega$ , both resonant, introduce a quadrupolar centrosymmetric excitation. A simple theoretical model of molecular orientation shows that these two last terms are detrimental for the building of a large  $\chi^{(2)}$ , except in the unique case of purely octupolar molecules, for which quadrupolar excitation is impossible.

Many experiments have been devoted to the study of the symmetry of the induced  $\chi^{(2)}$  as a function of the symmetry of light and of that of molecules. But very few of them have considered the competition with the quadrupolar order, which is a consequence of the saturation of the optical pumping process.

The photo-ordering processes are particularly efficient when the excitation by light produces a reversible photoisomerization and particularly with the well-known family of azobenzene derivatives (Trans-Cis photoisomerization). The understanding of the orientational mechanisms needs a spectroscopic study of the anisotropy of both isomers.

For all that reasons, we have built an experimental setup in order to measure the absorption of probe beams of different polarizations, propagation directions and wavelengths, during the AOP process. This experiment gives a dynamical and spectroscopic 3D characterization of the anisotropy, in correlation with SHG measurement. We will present the first results of this experiment, in comparison with theory.

The same experimental setup is also of interest in the case of photoinduced anisotropy in materials with liquid crystal properties. In this case the mesogenic effect produces a local order, either as microdomains or as a macroscopic order induced by the boundary conditions. Pumping by a polarized light modifies this order, but in general, the final order is not a simple copy of the symmetry of light and the dynamics of reordering is not easy to understand. Therefore, the 3D measurement of the anisotropy is of great interest, in this case also.

# Collision induced light scattering of SF<sub>6</sub> - isotropic and anisotropic spectra

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The study of collision-induced light scattering (CILS) intensities has been demonstrated to be a useful method to investigate multipolar polarizabilities in gaseous samples [1, 2]. In particular light scattering in noble gases and optically isotropic molecules has a collision-induced origin around the Rayleigh line. It is possible to study two kinds of collision-induced spectra: the anisotropic and isotropic ones. Generally the properties of scattering spectra obtained depend on the symmetry of the molecules involved. For an octahedral molecule, like SF<sub>6</sub>, for which the polarizability tensor is a scalar, the dipole-quadrupole multipolarizability tensor  $A$  vanishes and there is only one independent component of the dipole-octopole polarizability tensor  $E$ . For the anisotropic CILS from gaseous SF<sub>6</sub> most of intensities come from translational effects including the DID and electron overlap interactions.

The rototranslational contribution due to the dipole-octopole polarizability represent only a small part of the anisotropic intensities. In the case of the isotropic CILS spectrum of SF<sub>6</sub>, the DID interaction contributes only at the second order and this gives a good opportunity to study multipolar contributions and the dipole-octopole polarizability tensor in particular. Several papers were published concerning the collision-induced light scattering of SF<sub>6</sub> [3, 4]. They concern the anisotropic intensities in the frequency shifts range of 0-70 cm<sup>-1</sup>.

We present new experimental results of CILS intensities up to 210 cm<sup>-1</sup>. Experimental binary anisotropic and isotropic Rayleigh collision induced spectra of the gaseous sulfur hexafluoride are provided in absolute units. We discuss anisotropic spectrum in relation to the isotropic one. The isotropic binary collision induced spectrum was reported for the first time in a recent communication [5]. From comparison of experimental data with theoretical isotropic and anisotropic spectra of SF<sub>6</sub>, taking into account both translational (DID) and rototranslational contributions, a best recommended value of the independent component  $E$  of the dipole-octopole polarizability tensor is given.

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# Secure Holographic System with Polarization Encryption using Bacteriorhodopsin

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We have proposed a novel encrypted memory system using a polarization encryption technique, and have demonstrated this system using a polarization sensitive material bacteriorhodopsin.

The original image is represented as a two-dimensional polarization distribution and then is scrambled by a phase modulation mask. One cannot know the original polarization without information from the modulation mask.

After the encryption, the scrambled polarization distribution is recorded in a BR film that can generate a vectorial phase conjugated wave. When the polarization modulation mask modulates the relative phase difference between orthogonal axes, we can note that the decoding mask is complex conjugate of the encoding mask.

As the vector phase conjugate wave is transmitted through the same mask used in the encryption, the polarization modulation at the mask is exactly cancelled.

The vectorial phase conjugate reconstruction recovered the original polarization image successfully.

# STM-induced photoemission at solid- liquid interface

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Photoemission of a metal sample excited by a STM tip has been studied under UHV and in air for several years. We have extended STM-induced photoemission from metal surface to solid-liquid interface. A Au(111)-Au junction immersed in a liquid (hydrophobic, with a good electrochemical stability) droplet was studied with a home made STM. Five liquids were considered : octylbenzene, dodecan-4-ol, tetradecane, perfluorooctane and trichlorobenzene. The emitted light collected by a large aperture lens is detected by a silicon avalanche photodiode in single photon counting regime. Tunnel current characteristics  $I(V)$  and photon counting rates  $N(V)$ , as well as  $I(z)$  and  $N(z)$  ( $z$  being along the tip axe) were recorded on different points of the sample.

Similar counting rates were achieved with or without liquid. We have observed a decrease of the voltage threshold for photoemission when adding liquid compared to air medium. This is attributed to the decrease of energy of the radiative tip-induced plasmon in a medium with index of refraction higher [larger préférable] than one. We have also deduced from  $I(z)$  a strong decrease of the apparent tunnel barrier height, especially for perfluorooctane, which is a molecule very rich in electrons and which helps probably tunnel electron to go through the barrier.

Finally, we conclude that a liquid with a small index of refraction and which is rich in electron is convenient. Our observations permit to investigate the influence on STM-induced photoemission of a self-assembled molecule monolayer formed on a Au(111) substrate.

# Control of light emission properties of diodes by surface patterning

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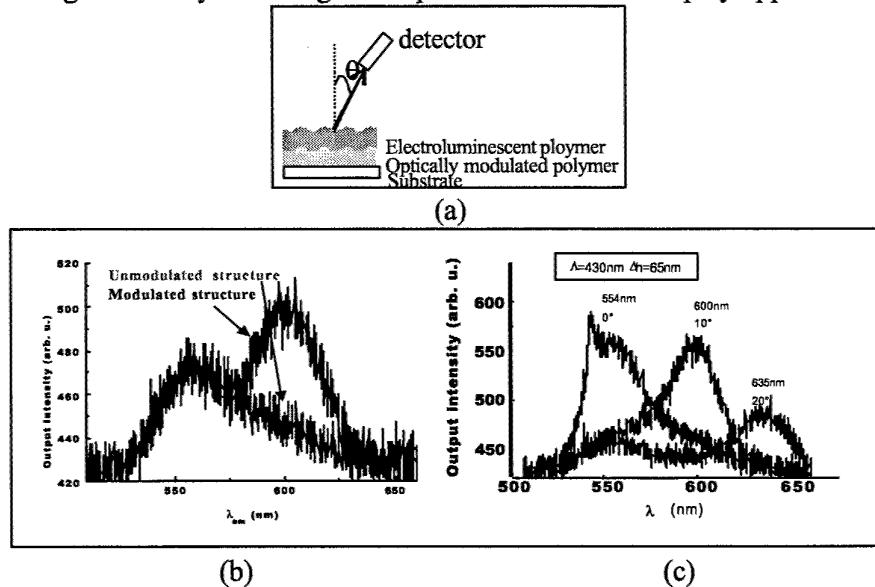
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With the realisation of devices ranging from filters to the well known DFB or DBR lasers, periodical patterning of the surface of polymer thin films appears to be a powerful method to control emission properties of luminescent layers. In this purpose new methods such as contact printing or molding, have recently been developed with the aim to provide a simple and low-cost way to pattern devices.

Here we propose an original one step structuration method towards the optimisation of the emission properties of devices such as organic light emitting diodes (OLED) in which a part of the light (about 80%) generated is lost by propagation into the diode structure.

The surface patterning is provided by means of a technique relying on photoinduced mass transport in a azo dye copolymer. Irradiation of the surface of such polymers using light interference pattern was shown to result in the direct formation of surface relief gratings with peaks corresponding to low intensity regions.

As a first step towards the realisation of a diode, the emission properties of a widely used electroluminescent material (Alq<sub>3</sub>) doped with rubrene evaporated onto both a modulated and an unmodulated area of the same substrate have been compared using an optical pumping. An important modification of the emission spectra depending on the emission direction jointly with an increase of the total amount of light radiated by the modulated sample is evidenced in the figure. The mechanisms responsible to such modifications are related to diffraction of part of light initially trapped into the layers. The possibility to increase the emission efficiency from devices consisting of thin layers is of great importance for future display applications.



transversal view of a modulated sample(a) and modification of light emission through structuration of the emitting layer at a given observation angle(b) and for different angles of observation(c). The grating period was  $\Lambda = 430$  nm, with modulation amplitude  $\Delta h = 65$  nm. The electroluminescent layer was the reference material Rubrene doped Alq<sub>3</sub>

# Donor-Acceptor Dyes for Advanced Photonic Applications

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Recently much research work has been devoted to investigate two- or multi-photon absorption of organic molecules, due to the growing interest in advanced photonic applications, such as laser scanning two-photon fluorescence microscopy, optical limiting, three-dimensional optical storage, microfabrication, and upconverted-lasing [1,2]. Organic push-pull compounds, with heteroaromatic rings acting as efficient acceptor (A) and donor (D) moieties, have been synthetized for second- and third-order non-linear optical (NLO) activity. Push-pull dyes, with general structure A- $\pi$ -D [2,3] allowed the preparation of highly efficient NLO-phores for frequency-upconverted lasing applications. Dyes, with the general structure A- $\pi$ -D- $\pi$ -A and D- $\pi$ -A- $\pi$ -D, show good two photon absorption (TPA) properties, largely exploitable for optical limiting applications [4].

The goal of our work is to characterize the nonlinear optical properties and to investigate the relation between the structure and the resulting nonlinear response. In fact, heteroaromatic groups offer the opportunity to vary widely the donor or acceptor strength as well as to add functionalities that favor the processing of these dyes into useful photonic materials.

Experimental measurements have been performed "step by step". Initially, the two-photon absorption (TPA) process has been investigated, through z-scan measurements, with nano- (ns) and femto-second (fs) laser sources. These excitation sources, with different laser pulse duration, allow one to distinguish between instantaneous contributions and sequential absorptions, which may follow the coherent TPA process, when ns pulses are used. The TPA spectrum has been measured, through pump-probe and z-scan measurements in a large visible range, in order to find the TPA peak wavelength. It turns out that, for our heteroaromatic dyes, TPA cross sections measured with ns and fs pulses differ by more than one order of magnitude and their wavelength dispersion is qualitatively different.

The characterization of the push-pull molecules, showing up-converted lasing properties, has been done by investigating the different steps of the up-converted emission process, with fs pulses at 790 nm. The TPA cross sections have been measured, with z-scan measurements. The one-photon fluorescence properties have been measured through fluorescence spectra and quantum yields. Finally the stimulated two-photon emission has been investigated by studying the cavity lasing using nonlinear transmittance measurements and emission spectra.

Together with the experimental measurements, theoretical models have also been used to explain the nonlinear optical behavior of these compounds. These models help in some cases to predict the nonlinear optical activity in order to provide guidelines for the synthesis and enhance the optical properties.

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# Charge Transfer in Molecular Logic Devices Possessing Different Molecular Bridges

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One of the advanced purposes in the design of molecular computing systems that are capable of conversion the photon energy. These supermolecules are designed from the photodonor and photoacceptor molecules joined with molecular insulator bridges. However, the above molecular bridges should be chosen by such way that the quantum yield for the charge separation process would be as high as possible. Thus, we intend to investigate the influence to charge transfer in photoactive supermolecules depending on the following molecular bridges: -N=N-; -CH=CH-; -CH<sub>2</sub>-CH<sub>2</sub>; -CH=N-.

The design of light-driven OR logically controlled supermolecular device based on the Disperse Orange 3 (DO3) and dithieno[3,2-b:2',3'-d]thiophene molecules (Fig. 1) was performed applying density functional theory (DFT) B3PW91/6-31G model. The above molecules are joined with different molecular bridges. The excited states of the supermolecular devices were investigated by using DFT Time Depended method.

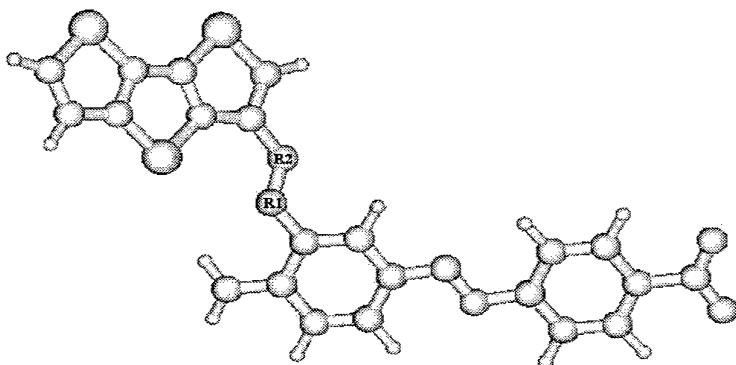


Fig 1. The molecular logical function OR designed from the DO3 and dithieno[3,2-b:2',3'-d]thiophene molecules where R1-R2 bonds correspond molecular bridges are -N=N-; -CH=CH-; -CH<sub>2</sub>-CH<sub>2</sub>; -CH=N-.

According to our investigations the different molecular bridges results to the shift of the absorption spectra of supermolecule. However, the first excitation of this OR device not depends on molecular bridge because in all possessing bridges the negative charge is transferred to the -N=N- molecular bridge that joins the phenyl rings of the DO3 molecule fragment. The second excitation of this supermolecule not depends on bridges and that corresponds the second excitation of the DO3 molecule fragment. Thus the photo *trans-cis* isomerization mechanism of the all OR logical device (supermolecule) should be the similar as isomerization of DO3 molecule fragment.

On the other hand, the transferred charge amount depends on molecular bridges. According to our investigations the molecular bridges with nitrogen atom (-N=N- and -CH=N-) and with double bond possessing bridge (-CH=CH-) decrease the amount of transferred charge.

# Dendritic polyesters for optical limiting applications

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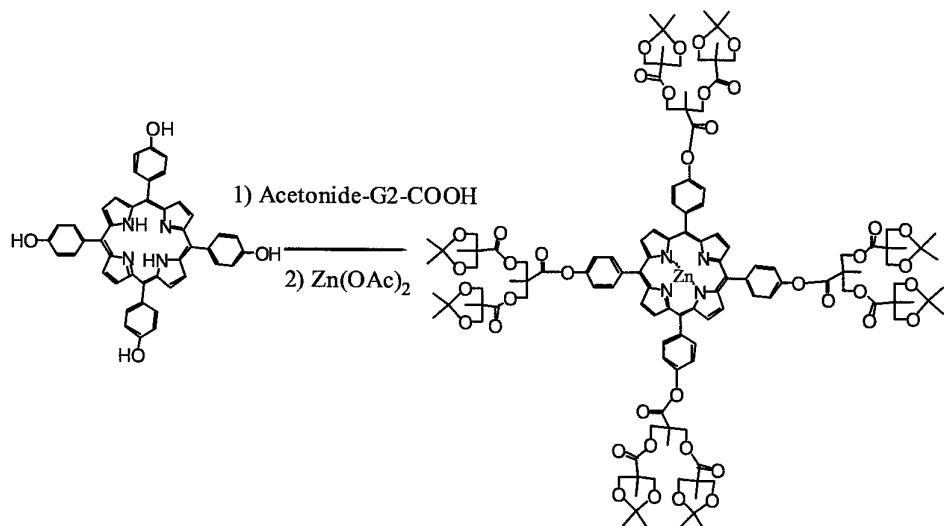
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Dendritic molecules [1] which are highly branched polymers, have showed a lot of interesting properties. Dendrimers can be used to increase solubility and they have also been shown to isolate the core moiety from the surrounding, suggesting that dendrimers can provide site isolation. [2]. The high degree of freedom in the molecular design of dendrimers makes them very attractive for use in photonic applications. The aim of this study is to show the versatility of the bis-MPA (2,2-bis(methylol)-propionic acid) based dendrons when used in optical applications.

**Dendron-decorated dyes for optical limiting applications.** In the protection against lasers, optical limiting (OPL) is an area of interest. We have explored the effect of using dendritic molecules as encapsulants of dyes having OPL-properties. In an initial study the OPL-dye of choice was a porphyrine. The synthesis was conducted according to a procedure described elsewhere [3]. Preliminary results indicate that the OPL-effect of the porphyrin is increased approximately by a factor 2 if the porphyrin is decorated with dendritic wedges. This is thought to be a result of isolation of the dye leading to extended life-times for the excited states, increasing the probability for multi-photon absorption. These and related results will be further discussed.



These results have encouraged us to try other dyes and the synthesis of a dendrimer-decorated thiophene is currently under way.

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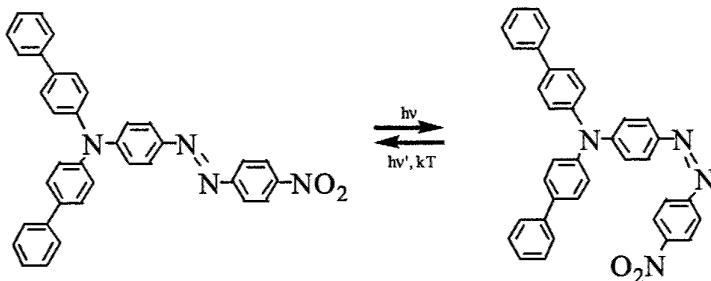
# Low-molecular-weight organic glass exhibiting photochromism and second-order nonlinear optical activity

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The conception of advanced devices realizing efficient high-speed image and data processing relies on the development of multifunctional materials. Organic molecular materials have appeared as very attractive candidates as their electronic, magnetic or optical properties tightly depend on their molecular structure. Actually, only scarce examples in the literature reported nonpolymeric amorphous molecules with glass transition temperature higher than room temperature in opposite to polymeric systems (polymers, sol-gels) which have been largely subjected to optical studies. Compared to organic crystals which are the archetypes of monomeric assemblies, the low-molecular-weight (LMW) monomeric glasses are easy to obtain and process for having handily materials. Furthermore, their weak tendency towards crystallization allows a high density of active chromophores and makes them very competitive to polymer systems where efficiency improvement through the increase of active-material concentration is cancelled by strong aggregation and phase segregation.

Our work focused on the synthesis and the optical studies of monomeric materials exhibiting both photochromism and second-order nonlinear optical activity which are involved in electrooptic modulators. Molecular design was based on a sterically demanding backbone (for forming stable amorphous materials) linked to a push-pull photoisomerizable moiety (for having dipolar molecular structure and photoisomerization properties). Following these requirements, we have synthesized a photoisomerizable azobenzene-type push-pull molecule which formed stable micrometer thick monomeric glasses ( $T_g = 92^\circ\text{C}$ ) upon spin-coating or vacuum vapor deposition.



The average surface roughness of the films has been found to be less than 0.5 nm by atomic-force measurements proving their high optical quality. Both relaxation kinetics after visible illumination and  $1.9\text{ }\mu\text{m}$  SHG properties have been investigated. The results pointed out a strong dependence on the film deposition technique. The thermal back reaction of the photoirradiated films was ten times slower for the evaporated films, which could be due to a higher molecular packing allowed through the evaporation process. Furthermore, the vapor vacuum deposited films exhibited spontaneous SHG, stable over one month at least, whereas the spin-coated films had to be previously electrically poled for generating a non-vanishing SHG signal. Major contribution to the SHG signal from the asymmetric organic layer-glass substrate interface has been ruled out as SHG intensity strongly depends on the organic layer thickness.

# NOTES



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## **NOTES**